RECENT ADVANCES IN THE CHEMICAL CONSTITUTION OF COAL

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The problem of chemical constitution of coal has long remained an intractable one but intensive work carried within the last decade in particular has steadily revealed important information on the structural pattern of coal. Since 1952 the concept of the structural parameters has emerged and, broadly speaking, whatever has been achieved so far mainly concerns this aspect of coal structure. By structural parameters is generally meant the state of combination of carbon, hydrogen and oxygen and their distribution in the average structural 'unit'. Such knowledge has been obtained from various physical studies e.g. x-ray[1-8], infra-red[9-11], nuclear magnetic resonance (n.m.r.)[12-14], proton spin resonance (p.s.r.)[15], electron spin resonance (e.s.r.)[16-18] and statistical techniques[19-23] involving density, refraction, sound velocity, magnetic susceptibility[24] and other properties.

Recently a number of chemical techniques[25-40] have been developed in these laboratories to assess the structural parameters in coal as revealed by physical measurements. In the main, these constitute oxidation, pyrolysis, and dehydrogenation and have led to important information on the state of combination of carbon and hydrogen in coal as well as on the size of the aromatic nucleus.

AROMATIC CARBON IN COAL:

Carbon is the predominant element in coal and the major part of it is believed[41] to be aromatic in character.

Two chemical techniques, namely, oxidation[25,28] and pyrolysis[31], have been employed by the authors for the quantitative measurement of the aromatic carbon. It is believed that by these methods of treatment the non-aromatic structure is preferentially oxidized or devolatilized leaving the aromatic skeleton of coal unaffected. It may as well be that the mechanisms of oxidation or pyrolysis of coal are not as simple as that. Hence, in more recent work[42,43] further support of the validity of the oxidation and pyrolysis techniques has been obtained by applying the methods on reduced coals. This is because in reduced coals the essential features of the original structure are believed to be retained, but the distribution of carbon and hydrogen in two forms, aromatic and non-aromatic, are altered.

A series of vitrains were reduced with lithium and ethylenediamine following the technique of I. Wender[44] and his co-workers. This treatment creates fresh hydroaromatic structure at the expense of the aromatics. The aromaticity of reduced coals can be theoretically calculated from the amount of hydrogen added during reduction provided that the aromaticity of the original coals as determined by chemical techniques are assumed to be correct. The aromaticity of the reduced coals as determined by oxidation as well as by pyrolysis studies have been found to be in excellent agreement with the theoretical values as reproduced[42-43] in Tables 1, 2.

Recent physico-chemical deductions[45,46,50,66,68] based on infra-red[4,9] and n-m-r[13-14] data especially those[45-46] put forward by the authors (Table 3) also give values of aromaticity which are in good agreement with those determined by the chemical methods of oxidation and pyrolysis (Fig.1). The values of aromaticity obtained by chemical techniques can perhaps be taken to be more precise than those deduced earlier by physical techniques.

Now that a precise estimate of aromaticity is available from chemical methods, it is of interest to compare such values with those earlier assessed by a number of physical techniques. Such comparison is depicted in Fig.2. It is found that the values of "ordered" carbon obtained by x-ray diffraction studies[3] closely fall in line with the most acceptable values of aromaticity, Assessment of non-aromatic structure and hence of the aromatic by infra-red studies is rendered difficult because of the lack of precise data on extinction coefficient ratio required for computation. Thus no firm values of aromaticity could be obtained by such methods. The preferred values of aromaticity obtained by I.G.C. Dryden[47] by a study of the self-consistency between several physical techniques are about 5 to 10 per cent higher than those directly obtained by chemical studies and cannot be reconciled with the values of alicyclicity obtained by the authors[37]. The values of aromaticity deduced by any of the statistical techniques made by van Krevelen and co-workers[19-23] are also 10-15 per cent higher than those obtained later by chemical techniques (Fig.1). Their values of aromaticity can also not be reconciled with the most preferred values of alicyclicity (determined in these laboratories), because the sum of the two exceeds the total carbon in coal (Table 4). If the amount of methyl carbon is taken into consideration the discrepancy would increase still further.

It will be of interest to note that the differences between values of aromaticity obtained by different techniques are greater in the case of coals of lower rank, but they tend to narrow down for higher rank coals. This may perhaps be explained by the inherent difficulties in the accurate measurement of the physical parameters owing to the possible interference by the presence of more oxygenated groups in coals of lower rank.

NON-AROMATIC CARBON IN COAL

(a) Alicyclic Combination

Information about the disposition and character of the non-aromatic carbon in coal has recently been obtained by the authors by a series of dehydrogenation studies[32-40]. It has been shown that the non-aromatic structure of coal is predominantly alicyclic.

The first estimates of alicyclicity[32-33] were obtained by employing Vesterberg's technique of dehydrogenation. The results so obtained were confirmed by another method of dehydrogenation with iodine. These estimates indicated that broadly 10-25 per cent of the carbon is in alicyclic combination in the bituminous range (carbon : 80-90 per cent). The alicyclicity progressively diminishes with increase in rank and is practically non-existent in the anthracite stage.

Subsequently, M.S.Peover[48] introduced the benzoquinone method of dehydrogenation and obtained much higher results. It has recently been shown by the authors[37] that the higher estimates of Peover may have been due to some systematic error in the polarographic determination of hydroquinone produced as a result of the dehydrogenation of coal. In fact, an investigation of the benzoquinone method in these laboratories has shown that the three methods of dehydrogenation viz. by sulphur, iodine and benzoquinone are comparable in so far as the extent of dehydrogenation possible in different ranks of coal (Table 5).

Further, the applicability of Vesterberg's technique in the dehydrogenation of coal structure has been corroborated by determination of hydroaromaticity in reduced coals. It has been found[49] that the freshly created hydroaromatic structure in the reduced coals undergoes dehydrogenation with sulphur quantitatively, apparently without any side reactions. These results are reproduced in Table 6.

Thus, the values of alicyclicity originally presented[32-33] from these

laboratories in 1958 should be treated as largely correct (Fig.3)*. In fact, the amount of hydrogen which could be added to coal at any stage of reduction could be quantitatively removed[49] during dehydrogenation with sulphur (Table 6). This indicates that coal structure is perhaps unique is its chemical reactivity and that the estimates of alicyclicity obtained by treatment with sulphur are possibly the maximum values.

An immediate consequence of dehydrogenation studies has been the recognition of the fact that the sum of aromatic and alicyclic carbon appears to be virtually constant at the level of 92 per cent of the total carbon in coal, irrespective of its rank, from lignite to the highest rank bituminous coal. The same conclusion repeatedly emerged from the pyrolysis studies on dehydrogenated coals and coals pre-treated with different chemical reagents[37]. The aromaticity progressively increases at the expense of the alicyclic structure, with increase in rank and this appears to be the principal mechanism[40] involved in geo-chemical metamorphism of coal in the bituminous range. The implications of this concept has been discussed elsewhere[40] and has possibly led to a better understanding of the pattern of coal structure and its variation during the genesis of coal. The physico-chemical deductions later made by A.F. Gaines[50] as well as by the present authors[45-46] (Table 3) also point to this constant feature of coal structure.

(b) Aliphatic Combination

As the aromatic and alicyclic carbon constitute about 92 per cent of the total carbon in coal, the aliphatic carbon would amount to about 8 per cent. Attempts made by several workers[51-53] to estimate the methyl groups in coal by employing Kuhn-Roth reaction have indicated that hardly 3-4 per cent of the carbon is possibly present in this form. This leaves another 4 per cent of the carbon unaccounted. From certain structural considerations the present authors suggested earlier that this unaccounted carbon could also be present[27,40] in the form of methyl groups. It is well-known that Kuhn-Roth method cannot be applied for the quantitative determination of C-methyl groups linked to aromatic structure and hence estimates of C-methyl groups by such procedure can only be minimum values.

From recent p.s.r. measurements made by Oth & Tschamler[15] it appears that 30-35 per cent of hydrogen may be present as constituents of C-methyl groups in coal. This is consistent with the authors' view that about 8 per cent of carbon in coal is present as methyl groups. Recent physico-chemical deductions[45] made by the present authors also lead to a similar conclusion (Table 3).

Nevertheless, direct experimental proof for the above supposition is yet to come. In this context the question of the probable presence of angular methyl groups in coal structure cannot be disregarded in view of strong indications for the same from dehydrogenation studies[33].

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* van Krevelen et al[67] had questioned the validity of Vesterberg's technique in the selective dehydrogenation of the alicyclic structure. Further studies[38,39] made since then indicated that side-reactions, if any, appeared to be minor and, accordingly, a revised estimate of minimum alicyclicity was presented. However in more recent studies[49] by the authors on reduced coals, it appears that, in so far as coal dehydrogenation is concerned, the Vesterberg's technique is possibly specific in the dehydrogenation of the alicyclic structure. A fuller account of the recent developments is being presented elsewhere[49].

HYDROGEN IN COAL

From chemical studies attempts have also been made to determine the different forms of hydrogen in coal, aromatic, alicyclic and aliphatic. Oxidation and pyrolysis techniques have enabled measurements of hydrogen broadly in two forms - aromatic and non-aromatic. Such measurements are not in good agreement with those assessed by infra-red studies. The discrepancy between these two sets of estimates is possibly due to inherent difficulties in the measurements of optical density and its interpretation which requires precise values for the extinction coefficient ratio. The estimates of aromatic and non-aromatic hydrogen made by the authors by oxidation and pyrolysis are mutually consistent (Fig.4). Further, it has been recently shown elsewhere[54] that the same techniques of oxidation and pyrolysis can also be successfully employed to determine the altered distribution of hydrogen in reduced coals. It may, therefore, be concluded that the variation of hydrogen in aromatic and non-aromatic form with increase in rank as determined by chemical methods by the authors can be considered the most acceptable at the moment. Such determinations were also reported by Van Krevelen[55] a few months later but only by the pyrolysis technique : his results are in agreement with the authors' values and are also shown in Fig.4. Probably re-assessment of the extinction coefficient ratio in case of infra-red results may reconcile the discrepancy between the two sets of estimates, made by physical and by chemical methods. J.K.Brown et al[10,11] have claimed to have given support to their preferred values of extinction coefficient ratio on the basis of recent studies on coal distillates, but such vacuum distillate of coal may not represent the coal structure. It has been earlier shown[34] by the authors (and which has been recently confirmed[56]) that such distillates primarily originate from the alicyclic structure in coal (Fig.5).

AROMATIC RING SIZE IN COAL

Coal is believed to have a polymeric or perhaps poly-condensate assemblage of structural units of varying dimensions. The measurement of the size of aromatic clusters in such structural 'units' is as important as the study of the state of combination of carbon and hydrogen. By oxidation studies the authors had also attempted an assessment of the average size of aromatic nucleii. According to the mechanism of oxidation suggested by the authors, the final oxidised residue of coal is believed to retain the aromatic skeleton of coal. Hence the atomic H/C ratio of the hypothetical unsubstituted aromatic skeleton corresponding to the oxidised coal would give a measure of the average size of the aromatic nucleii. It has been found[27] that the average size of aromatic nucleii does not vary much in the bituminous range (carbon : 80-90%) and is possibly constituted of 4 to 5 poly-condensed benzene rings per mean structural unit (Table 7). Earlier studies on x-ray diffraction[3] and on diamagnetic susceptibility[24] of coals led to similar assessments. Recent measurement of electron activation energy[58] also support the above estimates. In view of the consistency between the physical and chemical measurements (Table 7) it may, therefore, be concluded that possibly a fair estimate of the size of the aromatic units is now available.

Mild hydrogenolysis of coal extract, residue or coal itself by B.S.Biggs[59], B.S.Biggs and J.F.Weiler[60] as well as by J.Le Claire[61] had also led to the recognition (1936-37) that the 'units' of coal structure must be small in size. The isolation of dodeca- and tetradeca-hydrophenanthrene and hexadeca- and octadeca-hydrochrysene corresponding to 3-4 ring systems would now appear to be significant in the light of measurements of aromatic ring size by physical and chemical methods.

DISCUSSION

The techniques of selective oxidation and pyrolysis in conjunction with dehydrogenation studies have possibly yielded the most acceptable information on the state of combination of carbon and hydrogen as well as on the size of the aromatic nucleus. The knowledge that has been acquired is summarised in Table 8.

Perhaps the time has now come for reorientation of the studies on the consti-

tution of coal. There are still many gaps in our knowledge which have to be bridged before the macro-molecular structural pattern of coal can be precisely depicted. Such problems that remain to be solved are :

(i) Whether coal is a polymer in the typical sense;

(ii) If so, what is the nature of the polymer, especially the nature of linkage between the 'units' of coal structure;

(iii) The specific sizes of the individual structural 'units' of coal, in particular, the distribution of molecular weights among such 'units' which may not be all identical.

Information on the polymeric character of coal has been forthcoming from studies on solvent extraction and those on hydrogenolysis. R.A.Glenn and co-workers,[62] from a study of the liquid products obtained from hydrogenolysis, were led to conclude that coal structure has possibly repetitive units just as in a typical polymer. Confirmation of this polymeric concept has also possibly emerged from the recent studies of the authors[63] on the reaction of permanganate on coal. It has been shown that at any stage of degradation the residual coal left over after reacting coal with either acidic or alkaline permanganate retains virtually the same physical and chemical properties as that of the original coal (Table 9). This could perhaps be explained as a case of depolymerisation of the coal structure, followed by decomposition of the fragments into water soluble products like carbon dioxide, oxalic acid and benzene polycarboxylic acids.

The next stage is obviously to have adequate information about the actual repetitive 'units'. This can only be possible by isolation of the 'units' of coal by depolymerisation and determination of molecular weights of the 'units' thus isolated.

Another equally important knowledge to be sought is about the nature of linkage between the 'units'. Little or no information is available on this aspect at the moment. Studies on the mechanism of solvolysis of coal in organic solvents and of the dispersibility of coal in alkali (especially in lower ranks of coal) may reveal useful information.

In 1957 the authors[64] had indicated that the dissolution of lignite in alkali, even at room temperature is not merely a physical process but is probably preceded by hydrolytic splitting of bonds between the 'units'. It was suggested that in lignite (and in coal) the part that gives rise to humic acid and the residual part are possibly linked by flavone or similar type of linkage (e.g. pyrone, lactone, etc.) which are susceptible to cleavage in presence of alkali. However, it is premature to conclude anything definitely but it is believed that further work on these lines and others may throw greater light on this important aspect of coal structure. A fuller knowledge of the nature of the 'unaccounted' oxygen in coal vis-a-vis the dispersibility of coals in alkali, and of the mechanism of regeneration of humic acids from mature coals, may also be of help.

Besides the above basic considerations, we have yet to know more precisely about the character of nitrogen and sulphur. They are minor elements in coal but are believed to be integral parts of the coal structure. Information on the state of nitrogen has been scanty, though, of late, it has been suggested[65] that it may be largely present as functional groups. About sulphur, our knowledge is even less exact. The states of combination of these minor elements in coal are just as important as those of carbon and hydrogen.

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Table 1 - Verification[42] of the Oxidation Technique by the Determination of the Aromaticity of Reduced Coal Samples.

Sample No. & Particulars	%Analysis of the samples, d.m.f.			** H atoms added per 100 carbon atoms	% loss or gain on oxidation	Analysis of oxidised* samples, % d.m.f.					Carbon in oxidized samples, gm.		Aromaticity (C_{ar}/C)	
	C	H	O			C	H	O	O_{COOH}	C_{COOH}	Total	Corrected for C_{COOH} (C_{ar})	Found	** Calculated
1. Original	85.7	5.2	6.4	--	--	--	--	--	--	--	--	--	0.76+	--
1A. Reduced++	84.1	6.7	6.6	21	-12	63.5	2.1	32.2	19.0	7.1	55.9	49.7	0.59	0.55
2. Original	89.8	4.8	2.8	--	+7.4	73.1	2.1	22.3	13.0	4.9	78.5	73.2	0.82	--
2C. Reduced++	86.1	7.3	4.1	35	-22.2	61.4	2.2	34.2	18.6	7.0	47.8	42.4	0.49	0.47

* Oxidation done at 170°C for a prolonged period until there was no further oxidation. Generally this requires 1500 to 2000 hrs. in case of vitrains.

** Theoretical aromaticity calculated on the basis of hydrogen that was added during reduction.

\+ From pyrolysis; see Table 2.

++ Ethylene-diamine free analysis.

Table 2 - Validity[43] of the Pyrolysis Technique in the Determination of the Aromaticity of Coal.

Sample No. & Particulars	Analysis C %	Analysis H %	Analysis H/C	Pyrolysis(600°C) V %	Pyrolysis(600°C) F %	Aromaticity, C_{ar}/C "Experimental" (from fixed carbon)[31]	Aromaticity, C_{ar}/C Calculated from reduction data	Aromaticity, C_{ar}/C Calculated Statistical* method	$\frac{2(R-1)}{C}$ *
1. Original	85.7	5.2	0.73	26.8	73.2	0.76	--	--	0.51
1A. Reduced	84.1	6.7	0.95	48.5	51.5	0.54	0.54	0.54	-do-
1B. "	83.4	5.8	0.84	40.7	59.3	0.63	0.65	0.65	-do-
2. Original	89.8	4.8	0.64	14.9	85.1	0.87	--	--	0.49
2A. Reduced	87.9	6.3	0.85	39.0	61.1	0.63	0.65	0.66	-do-
2C. Reduced	86.1	7.3	1.02	57.1	42.9	0.48	0.49	0.49	-do-

* Assuming that the ring-condensation index, $\frac{2(R-1)}{C}$ of reduced coal would remain the same as in the original, the aromaticity of the reduced coals has been calculated from the formula : $fa = (1 - \frac{H}{C}) + 1 - \frac{2(R-1)}{C}$. For the computation of ring-index of the original coals, however, the aromaticity determined by pyrolysis has been assumed to be correct.

Table 3 - Non-aromatic Carbon-Hydrogen Distribution in Typical Vitrains*

(Reproduced in part from B.K.Mazumdar and A.Lahiri[45])

Rank	Primary Data				Deductions **								
					Non-arom. hydrogen			Non-arom. carbon					
% C d.m.f.	$+fha = \frac{C_{har}}{C}$	$C_{har} = C_{CH}+C_{CH_2}$ %	e (i.r.)	a (n.m.r.)	H_{CH_2} %	H_{CH} %	H_{CH_3} %	C_{CH_2} %	C_{CH} %	C_{CH_3} %	$b = \frac{H_{nar}}{C_{nar}}$	Aromaticity fa	Aromaticity + Alicyclicity fa + fha
82.5	0.25	20.6	0.23	0.88	2.12	0.66	1.22	12.7	7.9	4.9	1.89	0.69	0.94
85.0	0.22	18.7	0.26	0.95	2.04	0.54	1.39	12.2	6.5	5.6	1.93	0.71	0.93
87.5	0.17	14.9	0.35	1.06	1.80	0.34	1.56	10.8	4.1	6.2	2.10	0.76	0.93
90.0	0.11	9.9	0.54	1.25	1.38	0.14	1.58	8.3	1.7	6.3	2.30	0.82	0.93

* Deductions are shown in case of 4 out of 5 samples studied by Dryden[66]. The values of e, a and H_0 refer to his samples.

** Subject to the assumption that all the tertiary CH and secondary CH_2 groups are embodied in the alicyclic structures.

\+ Authors' maximum values of alicyclicity; see Fig.3 and also footnote in page 3.

Table 4 - Compatibility of the different estimates of aromaticity with those of alicyclicity.

Rank % C, d.m.f.	Aromaticity, fa		Preferred Values* of Alicyclicity (authors') fha	fa + fha	
	Statistical approaches (van Krevelen et al)[69]	Chemical approaches (authors)+		Van Krevelen et al's ++	Authors'
81.5	0.83	0.67	0.25	1.08	0.92
85.0	0.85	0.70	0.22	1.07	0.92
87.0	0.86	0.75	0.17	1.03	0.92
89.0	0.88	0.80	0.12	1.00	0.92
90.0	0.90	0.84	0.08	0.98	0.92

* from Fig.3. These values are considered to be the maximum; see footnote in page 3

\+ typical values from Fig.2.

++ the sum would still be higher if methyl-carbon is taken into consideration.

Table 5 - Comparative study of the three Methods of Dehydrogenation

Samples	Analysis		% of H removed during dehydrogenation		
	C	H	Sulphur (Vesterberg)	*Benzo-quinone	Iodine
Vitrains					
1	79.0	5.2	31	25	26
2	83.5	5.6	28	27	--
3	85.7	5.2	19	21	20
4	89.8	4.8	13	12	13
Reduced Vitrains					
1	86.1	7.3	43	44	--

* Authors' assessment.[37]

Table 6 - Selectivity of Sulphur (Vesterberg's) in the Dehydrogenation of the Hydroaromatic Structure in Coal[49].

Sample No. & Particulars	Analysis, d.m.f. C	Analysis, d.m.f. H	Yield of Reduced Vitrain per 100 gm. starting vitrain	* H added to aromatic positions per 100 gm. starting vitrain gm.	% of H removed by S (Vesterberg)	*Extra H removed in case of Reduced Samples	Alicyclicity, $\frac{C_{har}}{C}$ + Found	Alicyclicity, $\frac{C_{har}}{C}$ ++ Calculated
1	2	3	4	5	6	7	8	9
2. Original Vitrain	89.8	4.8		-	12.6	-	0.08	-
20. Reduced**	86.1	7.3	104.4	2.67	43.4	2.68	0.45	0.45
2.. Reduced**	86.1	5.9	104.3	1.30	32.1	1.28	0.26	0.25

* Compare column 5 with 7. This indicates the amenability of the hydroaromatic structure to complete dehydrogenation.

** Ethylene-diamine free yield and analysis.

\+ From the amount of H_2S formed without suspecting any side-reactions

++ The "theoretical" alicyclicity of reduced vitrains is based on the alicyclicity of the original vitrain and the extent of H-addition to it.

Table 7 - Average Aromatic Ring Size of Coal as Obtained by Different Approaches

Rank % C, d.m.f.	Aromatic ring size by oxidation technique[27,40]										No. of benzene rings per mean structural unit from		
	Analysis of the 'fully' oxidized coal										X-ray	Diamagnetic Susceptibility	Statistical methods (van Krevelen et al[69])
	C	H	O	O_{OH}	O_{CO}	O_{COOH}	O_{C-O-C}	H/C exp. atomic	Atomic H/C of unsubstituted aromatic nucleus of coal	No. of benzene rings per average structural unit.			
81.5	65.4	2.3	30.0	4.0	6.5	16.0	3.5	0.41	0.63	4			4.4
84.4	65.5	2.3	29.0	2.6	7.9	15.9	2.6	0.41	0.62	4			
87.3	67.6	2.2	28.2	2.2	9.0	14.0	3.0	0.39	0.60	4.5	2-5*	2-4	4.7
89.3	72.9	2.6	22.1	1.0	11.3	8.0	1.8	0.41	0.60	4.5			5.0
89.6	70	2.2	25.2	1.5	11.0	11.2	1.5	0.38	0.57	5			5.2
93.2	88.1	2.6	7.4	2.1	2.4	2.1	0.8	0.35	0.39	12-15	12		6.5

* This represents the range of assessment rather than the average size. Measurements have also indicated[3] that the average number of atoms per layer varies from about 14 atoms at 78% C to about 18 atoms at 90% C and about 36 atoms at 94% C. These would excellently correspond to the number of benzene rings per layer estimated from oxidation studies.

Table 8 - A Summary of the Essential Structural Parameters of Coal*

Typical Vitrains			Distribution of carbon			Distribution of hydrogen				
C %	H %	H/C	fa**	f_{har}**	f_{al} ($C-CH_3$) By diff.	*** H_0 %	$*\frac{H_{ar}}{H_0}$	$\frac{H_{har}}{H_0}$+++	$\frac{H_{al}}{H_0}$++	No. of benzene rings per mean structural unit.
81.0	5.4	0.80	0.67	0.25	0.08	5.0	0.23	0.45	0.32	4
82.5	5.3	0.77	0.68	0.24	0.08	4.9	0.25	0.42	0.33	4
85.0	5.4	0.76	0.71	0.22	0.07	5.1	0.29	0.41	0.30	4
87.5	5.3	0.73	0.75	0.17	0.08	5.2	0.33	0.35	0.32	4.5
90.0	4.8	0.64	0.82	0.11	0.07	4.7	0.46	0.20	0.34	5
93.2	3.5	0.45	0.97	nil	0.03	3.5	0.80	nil	0.20	12

* The distribution of C and H in different forms had also been earlier[33,39,40] presented but the present one is considered to be more accurate.

** maximum aromaticity and alicyclicity values from oxidation and dehydrogenation studies respectively.

\+ mean of physical and chemical determinations.

++ calculated from methyl carbon

+++ obtained by difference; this would be found to be largely consistent with the detailed distribution of hydrogen in CH and CH_2 forms recently deduced[45] by the authors from i.r. and n.m.r. data (Table 3).

*** % H less 'hydroxyl' hydrogen.

Table 9 - Comparative Analysis of Coals and Permanganate Treated Coals at different Stages of Degradation.

[Reproduced from A.Banerjee, B.K.Mazumdar and A.Lahiri[63]]

Sl. No.	Analysis of Coal, + d.m.f. C %	H %	Volatile matter (600°C)%	Nature of coke button (original coal)	Time of treatment with $KMnO_4$* in hrs. (at room temperature)	%loss of organic matter	Analysis of Treated Coal d.m.f. C %	H %	Volatile matter (600°C)%	Nature of coke button (treated coal)
1.	69.2	4.5	--	--	** 0.5	67.2	69.6	4.8	--	--
2a.	81.8	5.4	29.6	medium hard greyish bead	0.5	19.4	81.0	5.3	--	--
b.	"	"	"	"	1.0	25.9	81.6	5.5	30.4	weak but coherent
c.	"	"	"	"	2.0	36.3	82.1	5.4	30.1	-do-
d.	"	"	"	"	24.0	36.1	81.2	5.5	31.5	-do-
e.	"	"	"	"	** 0.5	27.0	81.3	5.4	--	--
f.	"	"	"	"	** 0.5++	83.1	80.0	5.5	--	--
3.	86.7	5.3	-	Highly swollen porous coke.	1.0	23.7	86.5	5.3	--	Medium hard porous coke
4a.	89.9	4.9	14.9	"	1.5	14.5	89.1	4.7	14.1	Highly swollen porous coke.
b.	"	"	"	"	2.5	14.3	89.3	4.7	14.8	-do-

+ All vitrain samples.

++ in contrast to the preceding experiment, in this case, more than 60% of the coal could be converted into soluble products because of 3 successive treatments of 10 minutes duration each, instead of a single treatment.

* different concentration of $KMnO_4$, alkali or acid and varying ratio of $KMnO_4$ to coal were used. This is of no consequence in respect of the analysis of the treated coals.

** dil. H_2SO_4 acid medium and the rest, alkaline.

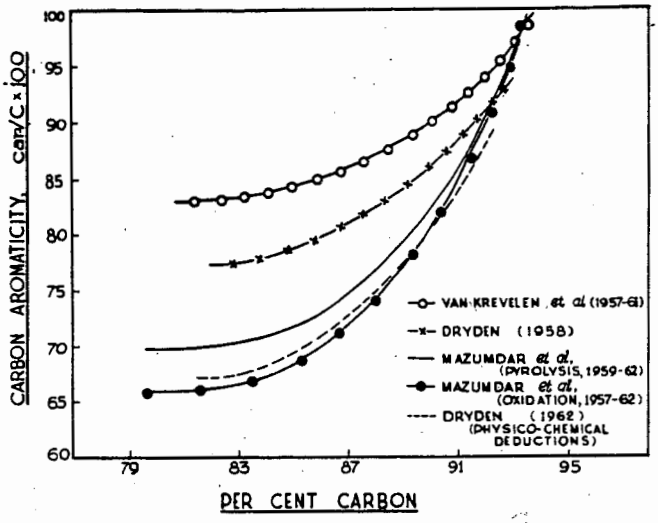

Fig.1 - Aromaticity of coal by different approaches.

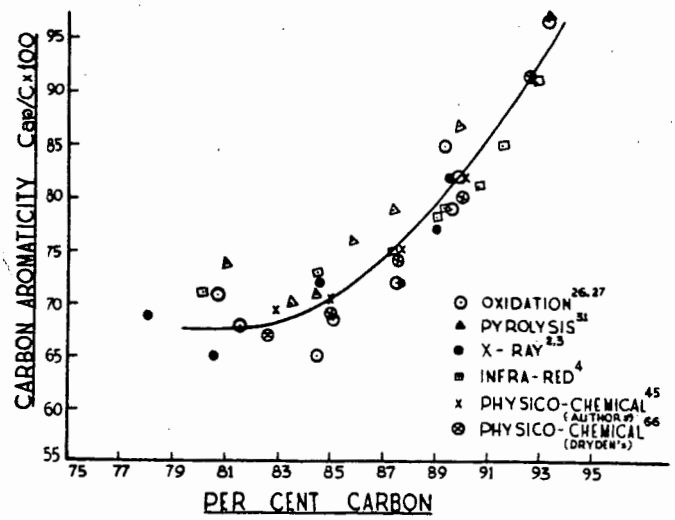

Fig.2 - Mean aromaticity of coal and its variation with rank as determined by chemical methods and its comparison with values from some of the physical and physio-chemical approaches.

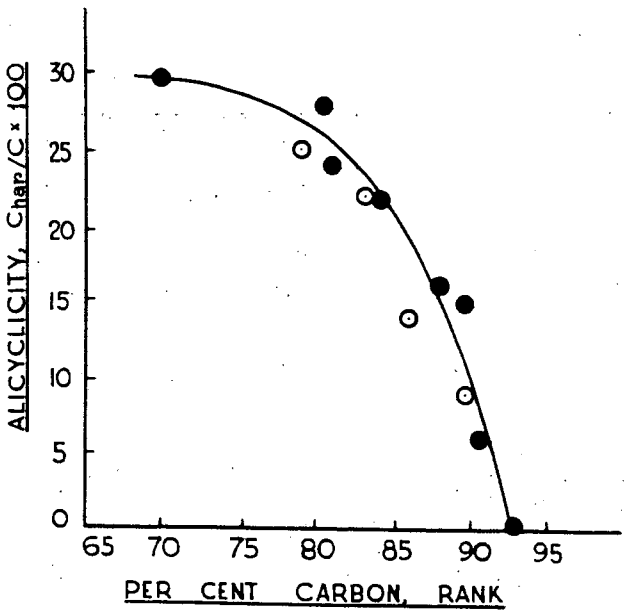

Fig.3 - Variation of the alicyclicity of coals with rank
● - values obtained in 1958 by dehydrogenation with sulphur[32,33]; ⊙ some recent determinations.

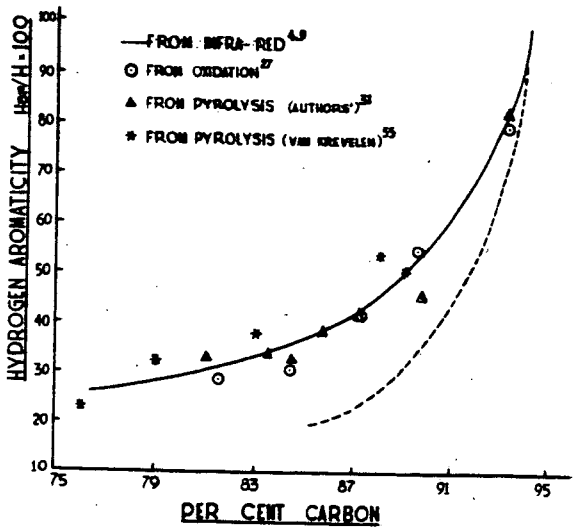

Fig.4 - Variation of the hydrogen aromaticity with rank : a comparison of the physical and chemical estimates.

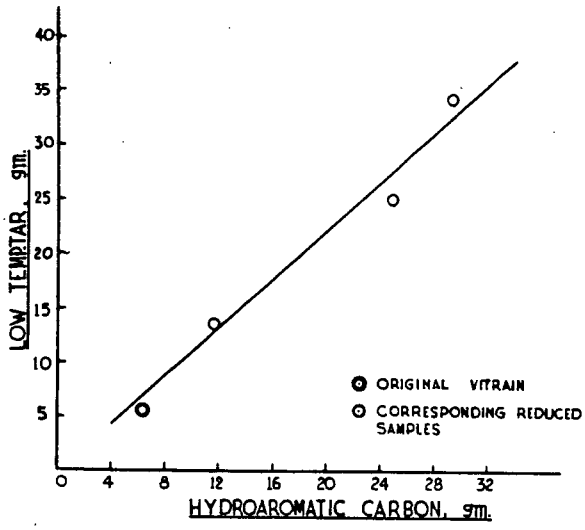

Fig.5 - Role of hydroaromatic structure in the formation of tar.
[Reproduced from Ganguly, S., Mazumdar, B.K. and Lahiri, A.[56]]

CATALYTIC DEALKYLATION OF TAR ACIDS

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Low-temperature carbonization has long been considered as a possible method for the utilization of lignite and other low-grade coals. Various fixed-bed processes were developed and tried prior to the first World War, but most of them met with limited success, and none became commercially significant. In the low-temperature carbonization process, the tar produced contains large quantities of tar acids. Depending on the coal carbonized and the conditions employed, the tar acids content of the tar will vary from around 15 to 50 percent. In the carbonization of Texas lignite, the distillable fraction of the low-temperature tar contains around 25 volume-percent tar acids of which only around 3 to 4 volume-percent are low-boiling phenols. The low-boiling tar acids, which are commercially obtained from coke-oven tar phenols, cresols, and xylenols have well-developed markets and uses and command a good price in the pure state. The market for the higher boiling phenols or tar acids is limited, and when marketed as impure mixtures, they sell at a much lower price than the lower boiling phenols. Owing to the limited market for these high-boiling phenols, large quantities of these coke-oven tars containing tar acids are burned as residual fuel. Using fluidized-bed techniques developed during the last decade in the petroleum industry, workable low-temperature carbonization processes have been developed and offer great potentialities, providing that the market value of the carbonization products can be increased, for example, by converting high-boiling tar acids to low-boiling phenols.

Low-temperature tars have a high degree of alkylation. Methods of removing some or all of the alkyl groups, or decreasing their chain length, consequently are of considerable interest. One method of conversion presently under study by the Bureau of Mines is the catalytic dealkylation at atmospheric pressure in which the alkyl groups are split off from the phenolic ring, yielding lower boiling homologs. Numerous catalysts of the silica-alumina type developed for petroleum cracking are available for study. The ideal catalyst would naturally be one that promoted cleavage of the alkyl group--aromatic nucleus carbon-carbon bond at the same time avoiding rupture of the phenolic carbon-oxygen bond, which would result in a high yield of phenol itself. The Bureau plans to test individual catalysts at three temperature levels to determine the most promising catalyst and the best temperature range, which will then be more comprehensively evaluated to fix optimum operating conditions for maximum phenol yield.

Three types of catalysts were used in Bureau tests performed in the laboratory glass reactor in which low-boiling methanol solubles were dealkylated. A silica-alumina catalyst in pellet form gave yields of light phenols of approximately 30 volume-percent of the feed acids. The same catalyst, crushed to 16-20 mesh,

showed somewhat greater activity and yields. With cobalt-molybdenum catalyst, yields of light phenols were very low, and large amounts of gas and carbon were produced. With a cobalt catalyst, a fair yield of light phenols was obtained even though the total conversion was low.

Experimental

Catalytic Dealkylation Laboratory-Scale Apparatus. The Bureau's laboratory-scale glass dealkylation unit was set up as shown in the schematic diagram (Figure 1.). A picture of the apparatus is shown in Figure 2. A calibrated feed reservoir of 250-ml. capacity was connected to a small bellows-type pump whose stroke could be adjusted to deliver from 15 to 3,000 cc./hr. of liquid feed. The pump discharged through a length of 1/8-inch stainless-steel tubing entering the reactor through a glass feed tube inserted in the top head of the reactor. An earlier feed device was tried, consisting of a 100-cc. hypodermic syringe mounted over the reactor and in contact with a motor-driven rotating threaded rod, which slowly depressed the syringe plunger. During operation, the plunger repeatedly stuck in the syringe barrel resulting in intermittent feeding and breakage hazards. This method was used in Runs 4 and 5, and was then replaced by the pump.

The reactor unit was of all-glass construction, designed as shown in Figures 3 and 4. The body of the reactor was a cylinder approximately 1-1/4-inch O.D. by 1-inch I.D. and 36 inches overall length, fitted at top and bottom with standard taper glass joints. It was fabricated entirely from "Vycor" 96 percent silica glass, affording safe operation up to 900°C. Eight inches from the bottom of the tube, indentations were made in the tube wall to hold a perforated porcelain disk, which served as a catalyst support. The reactor head, made of Pyrex glass, had three taper joints at the top. Through the central taper joint, a Pyrex thermocouple tube was inserted, extending lengthwise through the reactor tube and terminating at the porcelain support. The feed inlet tube fitted into a second joint; the third was not used. There were two small side connections with spherical joints, one for the entering of the carrier gas and the other for a pressure tap connected to a mercury manometer for measuring the pressure drop across the reactor packing. The bottom adapter, also of Pyrex, served to connect the reactor to the product receiver, a 500-cc. Erlenmeyer flask of actinic glass, immersed in an ice bath. Exit gases passed off through a small side tubulure and were metered through a wet-test meter. A tube packed with glass wool was placed in the off-gas line to protect the meter against dust or carbon particles and entrained vapors.

The reactor was mounted vertically within an electrically heated furnace, 31 inches overall length with a heating zone 30 inches long, rated at 2,200 watts and operable to 1,850°F. Temperature adjustment and control were obtained with a variable transformer in the power supply to the furnace. This furnace was installed after Run 22. Before that, two smaller 750-watt furnaces, each 13 inches long, were mounted end-to-end to encompass the reaction zone. With this arrangement, an unheated zone occurred where the two units came together, causing heat losses at that point, consequently, a poor heat transfer. A more uniform heating was obtained using the larger furnace.

Helium was used as the carrier gas to maintain flow throughout the system and to sweep feed and product vapors through the reactor. The gas was supplied from cylinders through appropriate regulators; the flow rate was measured by a

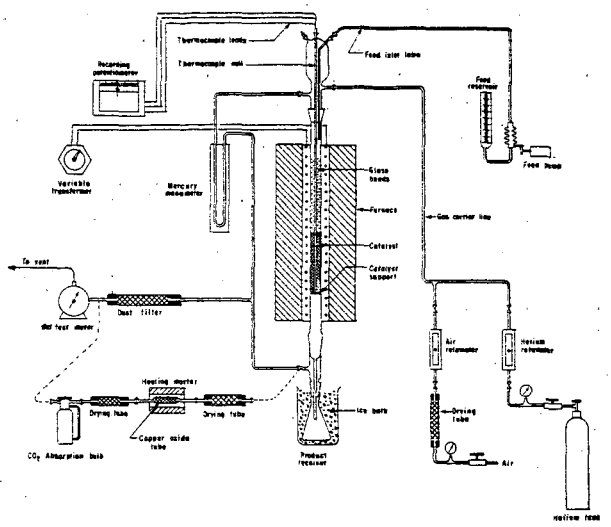

Figure 1. Schematic Diagram of the Laboratory Glass Dealkylation Apparatus.

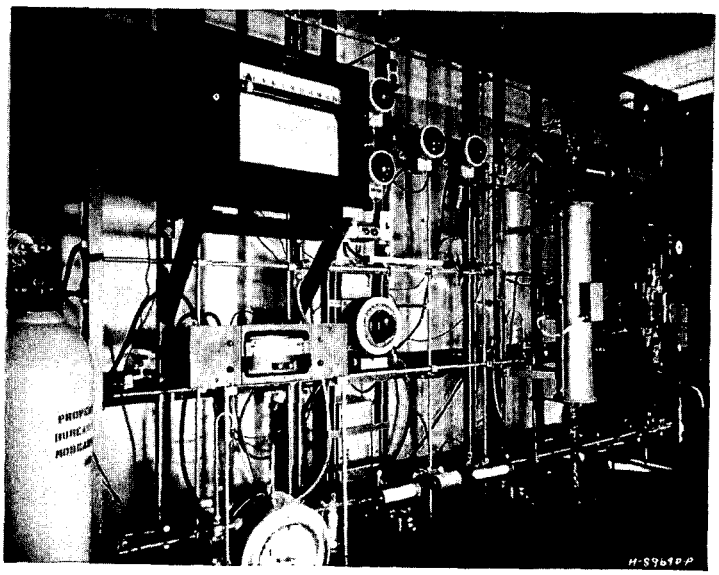

Figure 2. Picture of the Dealkylation Unit.

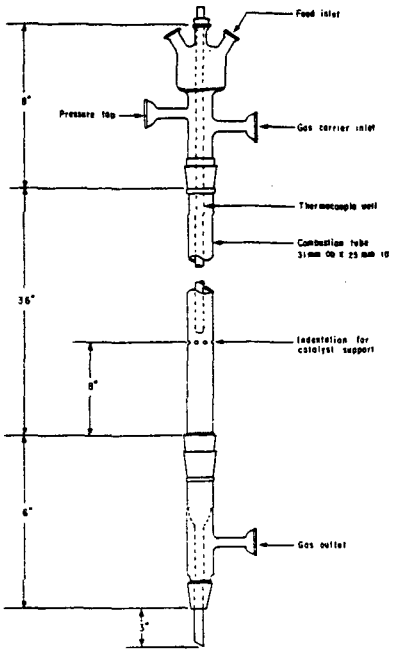

Figure 3. Dealkylation Glass Reactor.

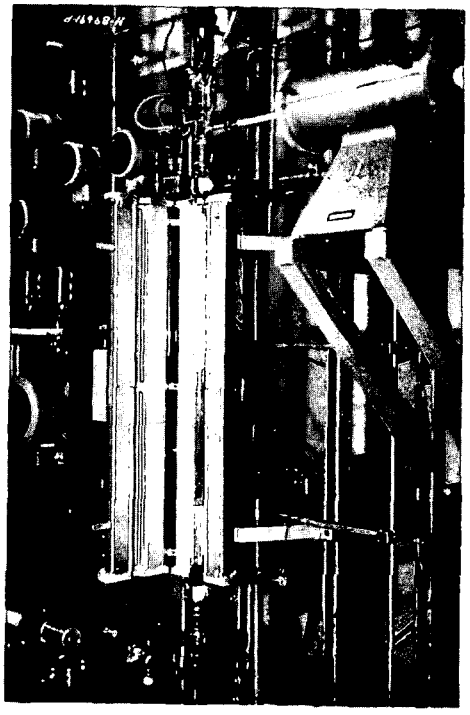

Figure 4. Picture of the Dealkylation Glass Reactor.

rotameter and was adjusted with a small needle valve at the rotameter inlet. Temperatures in the reactor were measured with chromel-alumel thermocouples connected to a Brown "Elektronik" six-point recording potentiometer. The pressure drop across the reactor packing, as noted before, was read on a mercury manometer connected across the inlet and outlet of the reactor.

In preparing for a test, the reactor tube and top head were assembled, and the thermocouple well was inserted. A weighed amount of catalyst was poured into the reactor through one of the openings in the top head. The height of catalyst above the support disk was measured, and the volume was calculated from calibration data previously obtained on the empty tube. Glass beads 4 mm. in diameter were poured on top of the catalyst to a convenient height, forming a preheating zone. The reactor was clamped into position within the furnace, and the necessary connections were made with the rest of the apparatus. Feed material was added to the feed reservoir. The specific gravity of the feed was determined at room temperature by weighing a graduated cylinder containing 100 ml. of feed.

Procedure. The tar acids for the dealkylation study were obtained from samples of low-temperature lignite tar supplied by the Texas Power and Light Company. The samples were products from a solvent extraction pilot plant in which hexane and methanol were used in a double-solvent operation to separate neutral and acidic components. Tar acids were recovered from the methanol extract by first stripping off solvent, then distilling the acids into two fractions designated as high-boiling and low-boiling methanol solubles.

We originally planned to use the total high-boiling methanol solubles for feed. This material was solid at room temperature and was therefore diluted with an equal volume of toluene to render it fluid and permit its pumping into the combustion tube of the glass reactor. With this feed, operating difficulties were caused by deposition of nonvolatile resinous substances, which plugged the reactor. Similar deposits occurred when a low-boiling methanol solubles residue boiling above 225°C. was used. Tar acids of intermediate boiling range did not cause any plugging. Because of its greater ease of handling, we decided to work with low-boiling methanol solubles. Samples of this stock were fractionated under vacuum on a Podbielniak high-temperature distillation apparatus using a 2:1 reflux ratio. The fraction boiling between 230°C. and 266°C. was retained as feed for the dealkylation study. In Runs 4 through 17, the feed was diluted with toluene; beginning with Run 18, the feed acids were used directly with no dilution (Table I).

The feed materials were analyzed for total acids by extraction with 10 percent caustic solution, considering the total caustic-soluble portion as phenols. The first batch of feed distillate showed 97.5 volume-percent tar acids, whereas the second batch analyzed only 82.0 volume-percent. A third feed fraction, not yet used, showed 81.0 volume-percent acids. The variation in the first material was probably owing to insufficient mixing before sampling, and for subsequent tests, the feeds should be fairly uniform.

Catalysts were commercial types furnished by various manufacturers. In most of the tests, a silica-alumina cracking catalyst, Socony-Vacuum TCC type 34 "Durabead," was used. Its composition is about 90 percent silica and 10 percent alumina, with less than 0.1 percent contaminants, which are primarily sodium salts. The catalyst comes in bead form and was sized to -4, +6 mesh before using.

Table I. Laboratory-Scale Catalytic Dealkylation of Tar Acids.

Run number	4	5	6	7	9	10	11	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
Catalyst type	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	b	b	b	c	c	c	d
Catalyst weight, g.	87.0	92.6	116.8	116.8	94.8	94.8	94.8	83.4	83.4	83.4	83.4	80.5	80.5	80.5	80.5	83.8	83.8	81.6	152.7	152.7	152.7	174.8
Catalyst volume, cc.	131	143	165	165	137	137	137	134	134	134	134	121	121	121	121	127	127	128	128	128	128	132
Condition of catalyst	New	New	New	Regen.	New	Regen.	Regen.	New	Regen.	Regen.	New	New	Regen.	Regen.	Regen.	New	Regen.	Mixed	New	Regen.	Regen.	New
Length of run, hrs.	1.08	1.55	3.00	2.67	1.08	1.58	1.58	2.08	2.12	2.00	2.10	1.17	1.55	0.92	1.80	1.63	1.60	1.70	1.50	1.45	1.50	1.35
Feed composition	e	f	g	g	g	g	g	g	g	g	g	h	i	i	i	i	i	i	i	i	i	j
Total feed, ml.	--	99	199	120	223	216	222	204	228	212	199	171	168	168	168	164	158	168	148	141	136	149
Total feed, g.	89	93	186	112	205	204	209	193	215	201	184	160	167	167	166	163	157	167	147	140	135	149
LHSV, vol. total feed/ vol. catalyst/hr.	--	0.44	0.40	0.28	1.51	1.00	1.03	0.73	0.80	0.79	0.71	1.21	0.90	1.51	0.77	0.79	0.78	0.77	0.77	0.76	0.71	0.84
Carrier gas flow rate, SCFH	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36
Operating conditions																						
Reactor ΔP, mm. Hg	1-9	0	0	0-5	0-65	0-50	0-98	0-48	0-68	0-18	0-74	0	0	0	0	3	3	2	0	0	0	0
Preheat temperature, °F.	--	800	539	683	489	543	607	844	891	839	843	456	640	518	748	724	781	507	569	615	727	643
Top catalyst temperature, °F.	839	--	825	824	842	783	835	712	702	759	711	688	699	675	703	703	746	703	788	704	860	762
Bottom catalyst temperature, °F.	840	800	826	823	813	800	847	821	821	825	825	829	829	825	828	825	903	754	832	754	906	831
Liquid product, ml.	--	86	181	101	201	204	205	189	214	194	180	160	154	164	158	149	138	157	124	122	109	139
Liquid product, g.	72	79	165	93	186	186	190	174	197	182	166	148	153	161	155	148	136	156	122	120	106	138
Carbon deposited, g.	--	6.83	11.53	9.81	7.03	8.32	5.63	7.90	8.81	7.22	8.75	4.49	6.58	5.69	6.66	7.05	9.04	5.73	19.30	15.40	21.0	14.38

a Socony-Vacuum "Durabead," silica-alumina, 4-6 mesh.
b Socony-Vacuum "Durabead," silica-alumina, 16-20 mesh.
c Girdler G-35B, cobalt molybdenum on alumina, 3/16" tablets.
d Girdler T-300, cobalt on kieselguhr, 1/8" tablets.
e 50 vol. % toluene + 50 vol. % 220-300°C. tar acids (100% acids).
f 50 vol. % toluene + 50 vol. % 230-300°C. tar acids (100% acids).
g 50 vol. % toluene + 50 vol. % > 225°C. LBMS-1 (98.0% acids).
h 50 vol. % toluene + 50 vol. % 230-266°C. LBMS-1 (97.5% acids).
i 100 vol. % 230-266°C. LBMS (97.5% acids).
j 100 vol. % 230-266°C. LBMS-2 (82.0% acids).

In Runs 21, 22, and 23, the catalyst was ground and a -16, +20 mesh portion was used. The two other catalysts used up to now were Girdler G-35B, in 3/16-inch tablets, containing 13-1/2 weight-percent cobalt and molybdenum on an alumina support; and Girdler T-300, in the form of 1/8-inch tablets containing about 60 percent cobalt on kieselguhr. All three catalysts were used as received.

Helium carrier gas was admitted to the system from the supply tank, adjusting the flow rate to 0.36 SCFH. Power was applied to the furnace and the temperature, as measured by the bottom catalyst bed thermocouple, was gradually raised to the desired operating temperature. When the temperature was stabilized at the desired level, the feed pump was turned on to start the run. The liquid feed stream coming into contact with the preheat zone vaporized and passed downward over the packed catalyst. The cracked vapors entered the product receiver, cooled by an ice bath, where the liquid product collected and helium and noncondensible product gases passed off to the gas meter.

The run was continued until sufficient liquid product was collected for analysis. Depending on the charge rate, a run lasted from one-half to 3 hours. Pertinent operating data were recorded on log sheets at 10 to 15 minute intervals. After feed was discontinued at the end of a run, helium flow was maintained, and the reactor was kept at temperature for about an hour to purge the reactor completely of all vaporizable products.

The total liquid product was weighed, its volume was measured at room temperature, and it was then distilled using a glass Vigreaux column 1/2-inch in diameter and 10 inches long. An initial fraction, boiling up to 160°C. (Table II) was distilled at atmospheric pressure. A second fraction with a boiling range of 160°-230°C. was distilled at 10 mm. Hg pressure. The tar acids content of this fraction was determined by extraction with sodium hydroxide solution. The amount of tar acids thus determined was considered the total yield of light phenols. Tar acids in the distillation residue were similarly determined. The acids in the caustic extract were recovered by neutralizing the extract with dilute sulfuric acid and were retained for possible future analysis.

During the cracking operation, considerable carbon was deposited on the catalyst. This carbon was removed by burning it off in an air stream, thus regenerating the catalyst. The reactor was brought to 1,000°F. on helium; air was then substituted for helium at a rate sufficient to maintain 1,050° to 1,100°F. during the regeneration. Carbon dioxide produced was absorbed in an absorption bulb packed with "Ascarite." The absorption bulb was preceded by a small tube, was packed with cupric oxide, and was heated to 700°C. by a small mortar, which converted any carbon monoxide to the dioxide. Drying tubes containing "Drierite" placed before and after the cupric oxide tube trapped any water vapor in the gas stream. The total weight of carbon dioxide formed was then taken as a measure of the carbon formed in the run, assuming that the catalyst deposit consisted entirely of carbon.

Discussion and Conclusions

The study on dealkylation of tar acids undertaken at the Bureau's Morgantown Research Center was concerned chiefly with the selection of a most effective catalyst for the production of low-boiling phenols and the examination of different variables in determining the maximum yield. This is a preliminary study. Not all of the

Table II. Fractional Distillation of the Dealkylated Tar Acids

Run number	4	5	6	7	9	10	11	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
Yields, wt. % of feed																						
Liquid product	80.7	85.1	88.8	82.5	90.7	91.6	90.8	90.2	91.5	90.4	89.8	92.7	91.8	96.1	93.5	91.0	86.7	93.8	83.3	85.5	78.5	93.1
Carbon	--	7.4	6.2	8.7	3.4	4.1	2.7	4.1	1.1	3.6	4.7	2.8	3.9	3.4	4.0	4.3	5.7	3.4	13.2	11.0	15.5	9.7
Gas + loss (by difference)	--	7.5	5.0	8.8	5.9	4.3	6.5	5.7	4.4	6.0	5.5	4.5	4.3	0.5	2.5	4.7	7.6	2.8	3.5	3.5	6.0	-2.8
Distillation of liquid product																						
IBP - 160°C., vol. %	--	68.7	60.9	64.3	56.8	53.2	58.6	59.0	53.3	59.2	57.2	56.7	7.5	5.5	7.6	9.8	14.4	7.1	9.7	7.4	13.5	6.3
160 - 230°C., vol. %	--	8.6	6.6	6.8	2.7	2.2	3.4	10.6	17.3	17.5	16.0	20.5	41.5	35.0	36.8	29.5	35.8	12.6	5.2	12.4	2.6	25.4
Residue > 230°C., vol. %	--	18.3	30.0	24.0	40.3	--	36.0	30.7	24.0	23.3	25.4	22.2	49.6	56.9	54.2	59.8	48.6	79.4	84.2	77.9	81.9	67.2
Tar acids in 160 - 230°C. fraction, vol. %	--	73.2	78.3	65.2	58.3	66.7	51.1	87.0	90.0	89.5	88.5	80.0	79.2	80.0	84.0	85.6	88.0	82.3	73.3	80.0	--	82.2
Tar acids in residue, vol. %	--	83.0	--	--	--	--	--	--	--	--	--	--	66.6	68.0	70.0	70.0	63.0	75.5	78.0	78.0	78.0	80.0
Total conversion, vol. % feed acids	--	73.6	--	--	--	--	--	--	--	--	--	--	68.9	61.4	63.5	60.9	72.6	42.5	43.6	46.1	47.6	39.0
Yield light phenols, vol. % feed acids	--	10.9	9.6	7.6	2.9	2.8	3.3	17.4	29.8	29.3	26.2	31.4	31.0	27.9	29.7	23.6	28.2	9.9	3.3	8.8	< 2.6	23.7

variables (such as temperature, space velocity, catalyst size, catalyst regeneration characteristics, type of feed stock, use of additives to feed such as steam or pyridine, etc.) were examined, and more research work will follow to study and determine the results of these variables.

The following conclusions can be drawn from the actual studies on the dealkylation of tar acids:

1. Tar acid feed stocks containing high-boiling residua are not suitable for dealkylation studies because they form nonvolatile, resinous deposits that plug the reactor. Fractions of intermediate boiling range did not form plugs, and successful tests were carried out using tar acids boiling from 230° to 266°C.

2. Silica-alumina catalyst, typified by Socony-Vacuum TCC-34 "Durabead," is very effective in dealkylation of high-boiling phenols to lower boiling homologs. Yields of around 30 volume-percent of feed acids were obtained operating at around 825°F. and with liquid hourly space velocities of about 0.8.

3. Girdler G-35B, a cobalt-molybdenum catalyst, appears unsatisfactory for dealkylation of tar acids because of low phenol yields and considerable losses of feed to carbon and gas.

4. A high-cobalt catalyst, Girdler T-300, showed possibilities of being highly selective in light phenol production, providing total conversion of feed acids can be increased.

5. The new laboratory-scale glass dealkylation unit (Fig. 1) has been shown to be suitable for carrying out catalyst screening tests and for future evaluation studies on individual catalysts.

Reference to specific commercial brands, materials, or models of equipment in this article is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

PROCESS CONDITIONS FOR PRODUCING A SMOKELESS BRIQUETTE FROM HOT CHAR

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PROCESS CONDITIONS FOR PRODUCING A SMOKELESS BRIQUETTE FROM HOT CHAR

1. INTRODUCTION

In the United Kingdom the implementation of the Clean Air Act of 1956 involves the setting up of an increasing number of smokeless zones throughout the country. In order to maintain sales of solid fuel, appliances to burn the present fuels smokelessly are being developed, and increased supplies of reactive smokeless fuels are being made available. To contribute to these supplies, a process for the production of a smokeless fuel from low rank coal has been developed at the Coal Research Establishment of the National Coal Board. A general account of this development has recently been given in another paper[1], and it is proposed here to review in detail some of the investigations which were carried out to determine the range of application and necessary process conditions.

The choice of low rank coal, volatile content greater than 35%, as a starting point is particularly appropriate in the U.K. as this material in small size gradings is economic to mine and well situated with respect to the markets.

To convert this material into a suitable smokeless fuel requires that it be both upgraded in size and rendered smokeless, without markedly reducing its reactivity. It was known[2][3] that low rank coal could be made smokeless by a process of partial carbonisation and it was thought likely that considerable reactivity would be retained in the char.

It was decided to attempt to briquette the char in the simplest possible way, i.e. without a binder of any kind. All attempts to briquette cold char using pressure alone have proved unsuccessful, but several attempts to briquette char when hot had shown promise.

Thus in 1931 Hardy[4], working in Belgium, took out his first patent on the hot briquetting of char and several more were filed, the last in 1937. The first Hardy patents cover a process which was intended to briquette finely divided coals and lignite; the raw coal was heated in a rotary oven to a 'plastic or globulated state', and compacted directly on discharge. The tars generated in the carbonisation process were claimed to act as binder.

Hardy's process was not a commercial success and in a much later assessment by Darmont[5] this was attributed to difficulties arising in the production of char under controlled conditions; agglomeration was a big problem. Similar difficulties seem to have been encountered by Piersol in his work in Illinois[6][7].

Interest in the briquetting of hot char was reawakened by Jappelt in 1952[8], who gave an extensive, though largely qualitative account of the factors involved in successful char briquetting. His work is of particular interest in that he concentrates on weakly caking coals, uses a rotary oven for preparing the char and advocates the use of an extrusion press for compaction.

In the light of these earlier investigations, the line of investigation adopted was to prepare the char under controlled conditions, and briquette it whilst still at a high temperature. This paper sets out to establish the process conditions for making a strong smokeless fuel from high volatile weakly caking coals by this method.

The strength of any compact produced by the direct briquetting of hot char can be expected to depend upon the following factors:-

1. The nature of the raw material.
2. The carbonisation conditions.
3. The compaction conditions.
4. The after-treatment or cooling of the briquettes.

It is not proposed in this paper to consider all the process variables, even if this were possible, but rather to focus attention on those which have been found to be the most important.

The paper first describes some of the laboratory investigations carried out under 1, 2, and 3 above, and later reviews these in the light of experience on a continuous plant. An account is then given of the necessary quenching conditions obtained from plant investigations. Finally after a brief sketch of the present state of the process a summary of the main findings is given.

2. LABORATORY INVESTIGATIONS

2.1. Description of Apparatus

The laboratory experiments were concerned with determining the conditions for the production of a strong briquette from char. It was not practicable to examine the conditions for the production of a smokeless product on this scale as insufficent product was available for test.

Fine coals (-10 mesh B.S.S.) of N.C.B. Coal Rank Classification Nos. 700, 800 and 900 (high volatile bituminous coals of low caking power) have been used; in coals of this type a reduction of volatile matter content to about 23% is sufficient to produce a completely smokeless char.

Preliminary experiments were conducted by heating a small briquetting mould ($\frac{1}{2}$ inch diameter) to temperatures in the low temperature carbonisation range (375-500°C) and introducing small charges of fine coal. After heating this material for about 5 minutes a plunger was introduced into the mould and the char was briquetted between the jaws of an hydraulic press. Strong compacts could be made in this way but this method of heating was not practical for commercial exploitation and, as the temperature of the material was not uniform, accurate temperature measurement was not practicable.

Experience at this research establishment had shown that low rank coals (CRC.700,

800 and 900) could be carbonised in this range with considerable accuracy of control using a fluid bed carboniser: the agglomeration problems had been overcome. Accordingly, a small laboratory reactor two inches in diameter was constructed which operated on a batch principle. In this reactor a coal charge could be loaded and carbonised at any temperature up to 550°C for any desired time. The char produced could be fed directly into a preheated mould and briquetted at any desired pressure.

The apparatus developed, which is illustrated in Fig. 1, was made up of the 2 inch fluid bed reactor which could be discharged into a 0.6 inch (dia.) heated mould held in the jaws of an hydraulic press. Fluidisation was normally carried out using nitrogen preheated to the chosen temperature of carbonisation and introduced into the base of the bed via the briquetting mould. Other fluidising gases, or mixtures of gases, could readily be substituted for the nitrogen flow. Control of the bed temperature was carried out by external heating and cooling coils wound round the reactor.

In operation both the reactor and the mould were first raised to the carbonisation temperature with hot nitrogen flowing through the system. A coal charge was then loaded into the carboniser and the heaters adjusted until the carbonisation temperature was reached: this took 2 to 3 minutes and thereafter the temperature was closely controlled (± 5°C) for the required carbonisation time. At the end of this period the fluidising flow was stopped, and the distributor plate opened to allow char to fall directly into the mould. The char was then briquetted. To prevent any surface oxidation each briquette was allowed to cool in a small closed container.

2.2. Testing Methods for Laboratory Samples

The quality of the briquettes was assessed by a destructive mechanical test. This consisted of a combined shatter and abrasion test in which single briquettes were first subjected to a standard abrasion treatment in a commercial abrader. The $+\frac{1}{8}$ inch material from this test was then dropped four times through a height of 6 ft., and the residue of $+\frac{1}{4}$ inch material weighed. This was expressed as the percentage of the weight of the initial briquette. The index so formed was regarded as a purely relative measure of briquette quality. In some experiments the density of the briquettes was determined before the destructive test.

2.3. Results of Laboratory Work

2.3.1. Nature of the Raw Material:

Whilst initial tests carried out with a single coal quickly confirmed that strong compacts could be made by heating the coal to temperatures in the range 375°C - 550°C andcompacting the char at 6 ton/sq.in., it was necessary at an early stage to know whether the process would be applicable to a wide range of low rank coals.

Samples of small coal, from six different collieries situated in the East and West Midlands divisions of the Board were selected and briquetted using carboniser temperatures between 375° and 475°C. The coal was ground to -10 mesh B.S.S., and the total residence time in the reactor was 8 minutes and the briquettes were made at a pressure of 6 ton/sq.inch.

The results of shatter and abrasion tests on these briquettes are shown in Fig. 2. Despite the fact that the samples ranged over different coal seams, had widely different ash contents (2 - 16%), and covered a volatile matter content range of 35 - 41% (see Table 1), the difference in briquetting performance between these samples was not significant.

In a later attempt to briquette as wide a range of materials as possible,

special maceral concentrates, prepared from a low rank coal by hand selection, were also examined. These covered a much wider range of materials than would ever be expected to arise from normal commercial preparation of low rank coals. It was found[9] for example that it was necessary to have inertinite concentrations of 60–70% before an unbriquettable material was obtained.

Size of grind can also be expected to affect the strength of char briquettes. Laboratory experiments have indicated that strength falls with increasing particle size.

To summarise, there is wide tolerance in the type of low rank material selected for the process provided that the material is crushed to a suitable size before briquetting (-10 mesh B.S.S. would appear adequate).

TABLE 1

Laboratory investigations of different coals – Details of coals used

Coal Sample			Gray-King Coke Type	Ash Content % (dry basis)	Volatile Matter Content % d.a.f.
Division	Colliery	Seam			
East Midlands	Bestwood	High Main	B	7.2	38.1
"	Calverton	High Main	A	11.7	36.8
"	Denby Hall	Mixed	C	16.5	37.8
"	Thoresby	Top Hard	D	10.9	35.6
West Midlands	Birch Coppice	Mixed	B	11.1	41.2
"	Dexter	Mixed	A	1.7	38.0

2.3.2. The Carbonisation Conditions

The results already obtained for different coals (Fig. 2) also show that at a residence time of 8 minutes the best briquettes are produced at a temperature of about 425°C.

The general effect of carbonisation variables on briquette quality may now be considered. Using fluid bed carbonisation the major variables can be considered to be the temperature of operation, the residence time of material in the reactor, and the nature of the fluidising atmosphere. In all these laboratory experiments the residence time was measured from the instant of loading the charge and thus also includes the heating-up period of 2-3 minutes.

These carbonisation variables were examined in two experiments. In each case Calverton coal C.R.C. No. 902 was used.

In the first of these an inert atmosphere (nitrogen) was used, briquettes being made over a range of temperatures from 350°C to 500°C and a range of residence times of 5 min to 80 min. Three replicates of this experiment were made, each replicate being suitably randomised.

The variation in density with temperature and residence time is shown in Fig. 3, and that of mechanical quality as given by the combined shatter and abrasion test in Fig. 4.

It may be seen that both mechanical quality and density are a maximum in the temperature range 400–450°C, and that both decrease with increase in residence time.

In Fig. 4 contours are included to show the residual volatile matter contents (dry ash free) of the briquettes. These indicate that the best briquette quality is achieved about the 30% volatile matter content, but that strong briquettes can be produced down to and below a 25% volatile matter content, at which level very little smoke emission would be expected.

Having established that it was possible to produce briquettes using an inert atmosphere in the carboniser, a second experiment was undertaken to test the effects of using other atmospheres. In all cases the same fluidising flows were maintained, and the atmospheres selected were:-

(i) Nitrogen as with the previous experiment.

(ii) Nitrogen/hydrogen mixture (90:10 parts by volume).

(iii) Steam.

(iv) Air/nitrogen (50:50 parts by volume).

The latter atmosphere was of particular importance in that in a continuous commercial reactor it was likely that the carbonisation heat would be obtained by heat of reaction, and air would be used as a fluidising gas. In the small reactor used, with the cooling coil working at maximum capacity the air/nitrogen mixture was the richest which could be used: at higher oxygen concentrations control was impossible.

With these atmospheres briquettes were prepared in the temperature range 400° to 500°C using residence times of 8 and 16 minutes. The results are given in Table 2. For all the atmospheres, the temperature range for good briquetting was found to be substantially the same, and the fall in quality with increasing residence time was confirmed. It may be seen, however, that briquette quality was significantly reduced when the air/nitrogen mixture was used for fluidising.

From these investigations it is clear that to produce strong briquettes long residence times in the carboniser must be avoided; briquettes must be made in a limited optimum temperature range, and reactions with oxygen in the fluidising gas must be kept to a minimum.

TABLE 2

Variation of Briquette Strength* with Fluidising Atmosphere, Carbonisation Temperature and Residence Time. (Laboratory Results).

Fluidising Atmosphere	Residence Time (min)	Carbonisation Temperature °C				
		400	425	450	475	500
Nitrogen	8	95	94	97	96	92
	16	92	95	94	94	53
Nitrogen/Hydrogen 90:10 parts (vol.)	8	92	97	96	96	95
	16	92	93	94	91	80
Steam	8	86	96	96	94	83
	16	81	92	93	88	38
Air/Nitrogen 50:50 parts (vol.)	8	85	89	91	87	83
	16	76	84	86	72	22

* Figures given are the percentages of +¼" material remaining after test.

2.3.3. The Compaction Conditions

It was mentioned in the introduction that char cannot be briquetted cold, and in the experiments so far described, care has been taken to maintain the briquetting mould at the carboniser temperature. Such a procedure may however be inconvenient on plant, and consequently a short investigation was made of the effect of cooling before briquetting. In this experiment briquettes were made using a single coal (Calverton C.R.C. 902) carbonised at 450°C for 15 minutes. After this period the char could be cooled to any desired temperature by switching over to cold nitrogen as fluidising gas, cutting the bed heaters, and turning on the external cooling. When the desired temperature drop had been achieved the char was then transferred to a mould maintained at the reduced temperature and briquetted (in this case at a pressure of 8 ton/sq.in.).

The results of the strength tests are shown in Fig. 5 where it can be seen that whilst quality falls slowly with temperature down to a temperature of about 250°C, after this point it falls rapidly.

The actual variation of compaction density with pressure is shown in Fig. 6, and it can be seen that at 6 ton/sq. inch the compaction curve is already becoming very steep at the temperatures involved. Pressures of 6–8 ton/sq. inch have proved adequate for all the coals studied both in laboratory and plant experiments.

3. SMALL SCALE PLANT INVESTIGATIONS

3.1. Description of Plant

A description of various experimental plants for the production of briquettes by this process has already been given elsewhere[1], so that it will only be necessary to add a brief description here. The particular plant used for most of these investigations was a small one capable of handling 100 lb coal/hour, Fig. 7. The reactor was 8 in. in diameter and was continuous in operation. Coal was fed into the vessel by screw feeder and char was withdrawn through a conical base to avoid agglomeration difficulties. It was normally run with cold air as the fluidising gas, all the process heat being derived by reaction with the coal.

Briquettes were made on an hydraulic extrusion press which normally produced a cylindrical compact 2 inches in diameter, and $1\frac{3}{8}$ inches long, this size being very suitable for domestic grates. With the limited plant throughput this size of briquette implies a briquetting rate of about 8 briquettes per minute, and thus speed of briquetting was low by commercial standards.

3.2. Testing Methods

As appropriate to this plant quality was assessed by larger scale tests, these consisted of:

(i) Shatter test - 10 lb. of product was dropped four times through 6 ft. on to a steel plate, and the weight percentages of +1 inch material determined; and,

(ii) Abrasion test - 5 lb. of product was subjected to 625 revolutions at a standard rate (25 r.p.m.) in a smooth steel trommel, the weight percentages of the resulting $+\frac{1}{8}$ inch material being determined.

For brevity in this paper the results of these separate tests have been combined in a single strength index by forming the product of the indices. This single strength index then bears some resemblance to the combined shatter and abrasion test results obtained from the laboratory investigations. Whilst the strength tests were intended for relative assessment of the product it is considered that where the index obtained exceeded 80% the briquettes would transport well, whereas if it was less than 50% they would transport badly.

3.3. Results of Plant Work

In the following review of the effect of process variables the product has in all cases been dry cooled (i.e. allowed to cool in sealed drums). On a full scale plant cooling in sealed drums would not be possible and development of briquette quenching methods is described later in section 3.3.4.

3.3.1. Nature of the Raw Material

Low rank coals from 24 different collieries were examined covering the range of Gray King coke types A to F. Using a temperature of 425°C and a residence time of 20 min, it was found possible, in all cases, to produce strong briquettes (i.e. combined shatter and abrasion index greater than 80%, see Table 3). At this carbonising temperature the smoke emission of the briquettes, as shown by tests in an open grate, was small in all cases.

TABLE 3

Plant investigations of different coals
Details of coals used and the strength of briquettes
Produced at 425°C

Coal Sample			Gray King Coke Type	Ash Content % (dry basis)	Volatile Matter Content % d.a.f.	Strength of bqs. made at 425°C (%)
Division	Colliery	Seam				
E.Midlands	Babbington	Deep soft	F	2.1	37.2	91
"	Thoresby	Top hard	F	5.2	35.3	93
"	Rufford	Top hard	E	4.9	37.7	93
"	Welbeck	Top hard	E	4.8	35.5	92
"	Babbington	Deep hard	D	3.1	35.9	92
"	Gedling	Top hard	C	6.0	38.8	92
"	Radford	Tupton	C	3.1	37.8	93
"	Shirebrook	Clowne	C	4.0	37.1	92
"	Whitwell	High Hazel	C	4.0	35.6	91
"	Bestwood	High main	B	7.5	37.8	91
"	Bestwood	Main bright	B	1.5	38.5	92
"	Gedling	High Hazel	B	6.5	39.8	93
"	Ollerton	Top hard	B	5.2	37.9	90
"	Warsop	High Hazel	B	9.1	36.3	91
W.Midlands	Coventry	Mixed	C	1.9	39.4	91
"	Haunchwood	Mixed	B	5.6	40.7	90
"	Newdigate	Mixed	B	2.9	39.1	92
"	Arley	Mixed	A	5.0	39.2	91
"	Dexter	Mixed	A	4.2	36.8	89
N.Eastern	Kiveton Park	High Hazel	F	2.7	36.1	87
"	Markham Main	Barnsley	D	3.8	36.8	90
Scottish	Dalkeith	Barrs	C	5.0	41.0	89
"	Dalkeith	5 ft	C	4.8	40.6	90
"	Dalkeith	6 ft	C	3.8	40.0	91
"	Woolmet	Ell	B	3.1	36.8	89

The pressure required to make these compacts was about 6 ton/sq.inch, although for the higher coke types somewhat lower pressures were often adequate.

The plant results therefore show that the hot char briquetting process is applicable to a wide range of low rank coals, and thus confirm and extend the earlier laboratory findings.

3.3.2. The Carbonisation Conditions

The plant investigation of the effect of carbonisation variables on briquetting has been rather more restricted because of plant limitations than that in the laboratory. An investigation using Dexter coal, C.R.C. No. 902, has, however, been made of the variation of briquette quality with temperature (in the range 375°C to 450°C), and residence time (15 min to 45 min). In order to achieve the longer residence times it was necessary to dilute the fluidising air with nitrogen, although on a larger plant a deeper bed could be used.

The results of combined shatter and abrasion tests carried out on briquettes made using a constant pressure of 7 ton/sq. inch for the above range of carboniser variables are given in Fig. 8. As with the laboratory results it may be seen that the strongest briquettes are made in the range 400°C - 450°C, and that quality diminishes with increasing residence time.

As with the laboratory briquettes the volatile matter content for optimum strength is higher than the 23% at which the char is completely smokeless.

3.3.3. The Compaction Conditions

In the laboratory it was shown that any substantial reduction of temperature between carboniser and press produces a weaker briquette.

Tests were carried out on the plant by removing heating and lagging from the short feed line connecting carboniser and press. The briquetting temperature as indicated by thermocouples in the char stream are given in Table 4, together with the shatter and abrasion indices of the briquettes produced.

TABLE 4

Variation of Briquette Strength* with Briquetting Temperature. (Plant Results)

Carbonisation Temperature	425°C
Briquetting Temperature	Briquette Strength*
425°C	93
400°C	87
350°C	84
285°C	83

* Results quoted are the combined plant shatter (+ 1") and abrasion (+ $\frac{1}{8}$") test results.

\+ All briquettes were prepared at a pressure of 7 ton/sq. inch.

Over the limited range of temperature drop investigated in this way there was a reduction in quality with increasing temperature drop; this confirmed the laboratory results. It is preferable to permit no fall in char temperature between the reactor and the press: indeed there may be a case for using a rising temperature gradient.

With respect to other briquetting variables it has been found on the plant that density increases with pressure, but that the rate of increase falls at higher pressure, as would be expected. This is true also of briquette strength, but on extrusion presses another effect is important. At high pressures the separation between successive briquettes becomes poor, and in some cases continuous lengths of undivided briquette emerge from the nozzle. For briquette appearance it would thus appear that pressures which are too high can be a positive disadvantage and this seems to be particularly the case with the more highly caking coals. However, wherever this phenomenon has been encountered it has been found possible to make strong briquettes at pressures below those which bring about severe sticking.

3.3.4. Quenching Conditions

In bulk production of char briquettes it is necessary to introduce a cooling stage to prevent spontaneous combustion of the product and it has already been pointed out that, in the assessments so far of process variables, the product has been dry quenched in sealed drums. Cooling in this way takes between 12 hours and 2 days, depending on whether 90 lb or 250 lb drums are used.

Quite early in these investigations wet quenching by immersion in water was considered as an alternative. By this means briquettes can be quenched to a safe temperature (i.e. about 50°C) in 20 min., but such cooling produces internal cracking and gives substantially lower shatter indices than those obtained for a dry cooled product. This is particularly true for briquettes produced at 425°C, and for the more highly caking coals.

Experiments on cooling briquettes in fluid beds of cold sand and in dry ice quickly demonstrated that the rate of cooling rather than the nature of the coolant was responsible for the cracking.

When a briquette emerging from a press at about 400°C is plunged directly into cold water it suffers a large thermal shock. The shock can be reduced by cooling the briquettes more slowly, either in an inert atmosphere or by spraying lightly with water, prior to complete immersion. That such a two-stage cooling procedure reduces internal cracking is illustrated in Fig. 9, where sections of briquettee dry cooled in sealed tins for 10 and 20 min. before immersion in water are compared with briquettes which were immediately immersed.

Plant investigations have shown that it is desirable to reduce the average temperature gradually to about 150°D before immersion in water. The first cooling stage can be performed by cooling on a conveyor in a steam atmosphere for 30 min., or by a shorter period, (15 min.) of spray quenching (see Fig. 10), followed by 8 min. immersion in water. These two-stage treatments gave briquettes closely comparable in strength with those cooled in sealed drums. For commercial exploitation, steam cooling, followed by water immersion, is preferred.

3.3.5. Smoke Emission & Fuel Performance

With the greater supply of product from the plants it was possible to carry out open, i.e. stool-bottom, grate tests[10] and coke grate tests[11] for radiation and visible smoke. Smoke emission may be measured optically using a photo-electric cell to measure the obscuration of a light beam traversing the flue or the smoke may be collected in an electrostatic precipitator and weighed. The second method is likely to be accepted as a British Standard method but for our purpose the convenience of the optical method outweighed the rather better accuracy of the gravimetric method.

Optical smoke indices are given in Table 5. Values obtained from other "naturally smokeless" coals are included for comparison. The parent coal, in this case Dexter C.R.C. No. 902, gave an index of 93.

It can be seen that smoke emission decreases rapidly with increasing carbonisation temperature and decreasing volatile matter content until the product becomes virtually smokeless at 23% volatile matter content. Further, the range of smoke emission of the "naturally smokeless" fuels given in Table 5, is wide enough to give considerable latitude in process conditions for the production of a strong briquette.

TABLE 5

Smoke Emission Indices for briquettes burned in stool-bottom and coke grate tests

a) Smoke index of briquettes made from Dexter char; 30 min. residence time in carboniser.

Carbonisation temperature °C of the briquettes .	375°C	400°C	410°C	425°C	450°C
Volatile matter content d.a.f. of the briquettes	32.3	27.9	26.0	23.4	21.0
Smoke emission index in stool-bottom tests	23	10	4	2	< 1
Smoke emission index in coke grate tests	18	13	5	2	< 1

b) Sample smoke indices of other coals for comparison

(i) Stool-bottom grate

			Index
International coal	16.5% V.M. d.m.m.f.	(3" x 2")	35
Deep Navigation coal	14.0% V.M. d.m.m.f.	(3" x 2")	7
Penrikyber coal	12.7% V.M. d.m.m.f.	(3" x 2")	3
Commercial Low Temperature Coke		(+ ¾")	3

(ii) Coke Grate

International coal	16.5% V.M. d.m.m.f.	(2¼" x 1¼")	33
Deep Navigation coal	14.0% V.M. d.m.m.f.	(2¼" x 1¼")	8
Penrikyber coal	12.7% V.M. d.m.m.f.	(2¼" x 1¼")	4
Commercial Low Temperature Coke		(+ ¾")	2

The critical air blast test[12] showed the fuel to be "reactive" in that the required air blast was less than the minimum flowused in this test (0.008 cu. ft. air/min). The general performance of the briquettes in stool-bottom grate tests is illustrated in Table 6; it can be seen that, apart from smoke, the performance of the briquetted fuel equals that of the parent coal.

TABLE 6

Performance of Dexter coal and Dexter char briquettes in stool-bottom grate tests*

Fuel Tested	Dexter 2¼" x 1¼" coal	Dexter Char Briquettes (425°C)
Time to reach 6,000 B.t.u./h after ignition (min)	28	29
Peak radiation after ignition B.t.u./h	10,410	8,060
" " " 1st refuel "	10,530	9,940
" " " 2nd " "	9,140	9,990
" " " 3rd " "	8,550	9,130
Gross radiation (2000-2000 B.t.u./h) B.t.u.	67,380	69,070
Average radiation per hour "	6,670	6,470
" " " pound " of fuel burned	2,900	3,020

* In the stool-bottom test a fire is lit using 9 lb. of coal and recharged three times using 5 lb. of coal per refuel.

4. DISCUSSION

So far we have reviewed some of the main process variables involved in briquetting hot char in an extrusion press as revealed by laboratory and small pilot plant investigation. We have shown that a strong briquette can be made and that there is a fair range of conditions under which the briquette is also smokeless, but we have not considered some of the variables which are of great importance to the commercial success of the process.

First is the ability of the carbonising and briquetting systems to operate continuously over reasonable periods without shutdown. The carbonising system is particularly prone to troubles associated with agglomeration in the bed and the extrusion press is susceptible to high rates of die wear. In order to get some measure of these likely difficulties a 500 hr. run on an 18 in. dia. carboniser/2" dia. extrusion press rig was attempted. Only minor difficulties were encountered in the carboniser and die wear was found to be much less troublesome than had been expected.

For commercial use it is necessary to operate the extrusion press at much higher speeds than is possible on small pilot plant where the limit was about 40 strokes per minute. The limit was set primarily by the capacity of the carboniser but was also influenced by the transient shock waves which are characteristic of hydraulic presses operating at high speed. Recent experience on a variable speed mechanical press, Fig. 11, has shown that good briquettes can be made at speeds of 80 strokes per minute, and that higher speeds may well be possible. Attempts have also been made to briquette the char on roll presses, these have been successful but demand very close control of carboniser conditions.

Briquette shape is important commercially and some of the variants possible on an extrusion press are illustrated in Fig. 12. In order to obtain optimum fuel performance on an open fire, briquette weight should not exceed 100 grms.

Tonnage quantities of briquettes have been made for market and transport trials, and Fig. 13 gives some idea of the appearance of a wagonload of dry quenched briquetted after a transport test.

The fuel has been shown to be an acceptable premium grade smokeless fuel for the domestic market. It is smokeless at volatile contents between 23 and 26% and is made without unpleasant and expensive binder. Preparations for commercial development are already in an advanced stage. It remains to exploit the virtues of this process in the manufacture of closed stove and metallurgical fuel, and to extend the range of coals which can be processed in this way.

ACKNOWLEDGMENTS

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The views expressed are those of the authors and not necessarily those of the Board.

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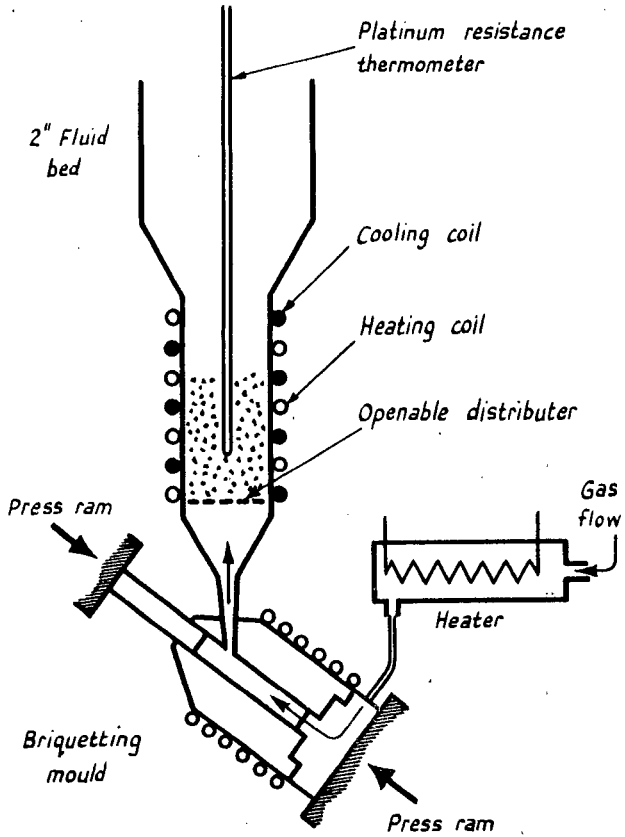


FIG. 1. LABORATORY BRIQUETTING APPARATUS

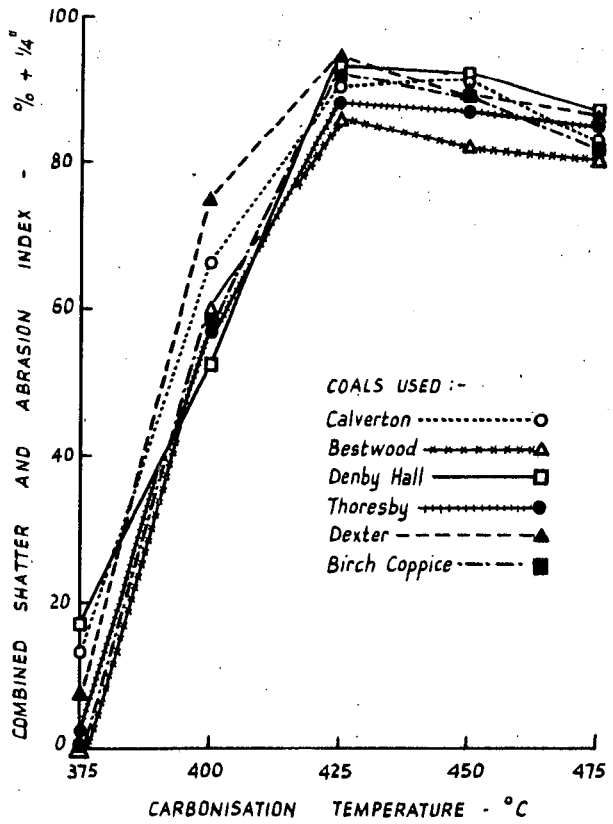


FIG. 2. BRIQUETTING PERFORMANCE OF SIX LOW RANK COALS.

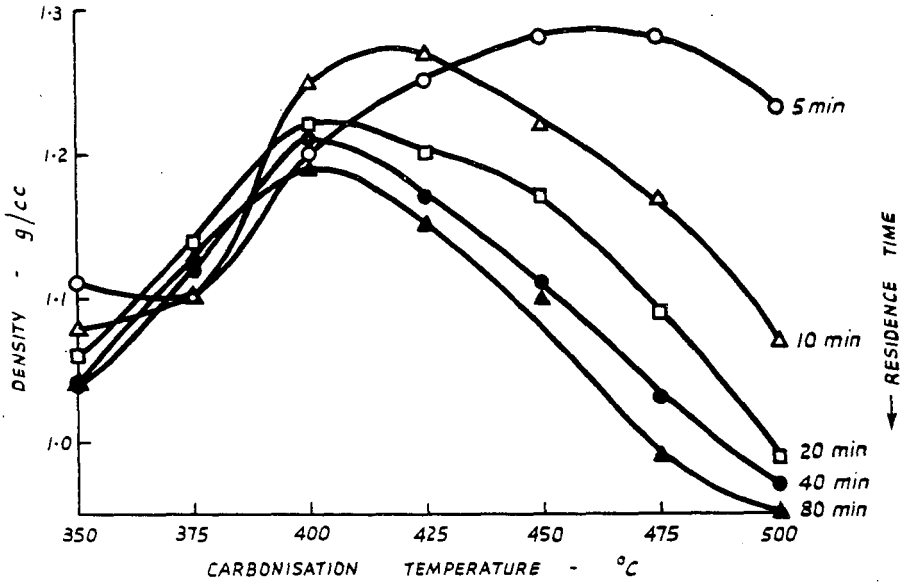


FIG. 3. VARIATION OF DENSITY WITH TEMPERATURE AND TIME.

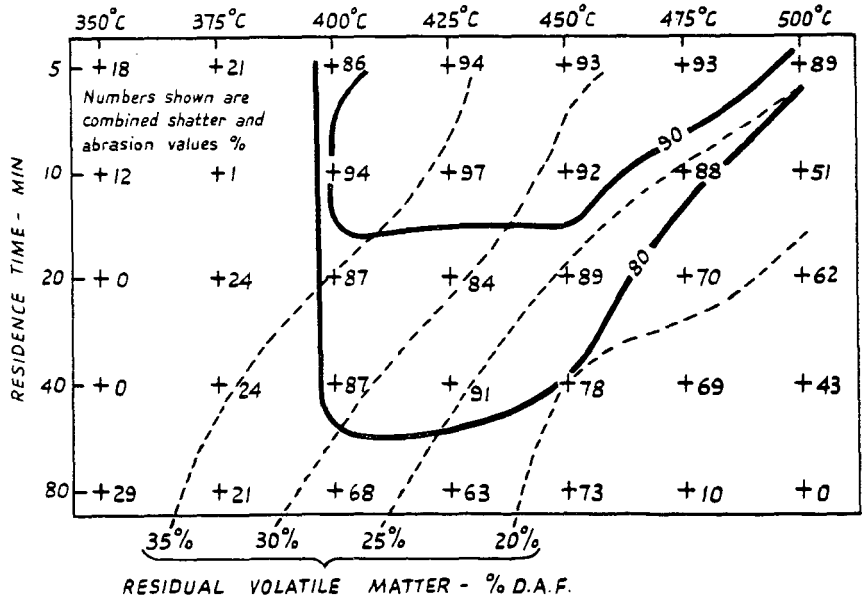


FIG. 4. VARIATION OF STRENGTH WITH TEMPERATURE AND RESIDENCE TIME. (LABORATORY RESULTS)

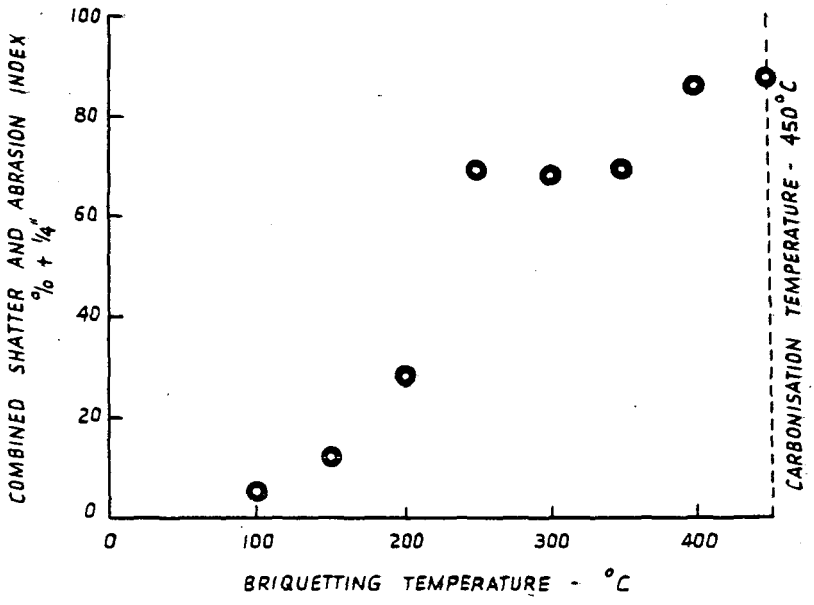


FIG. 5 EFFECT OF BRIQUETTING TEMPERATURE ON STRENGTH.

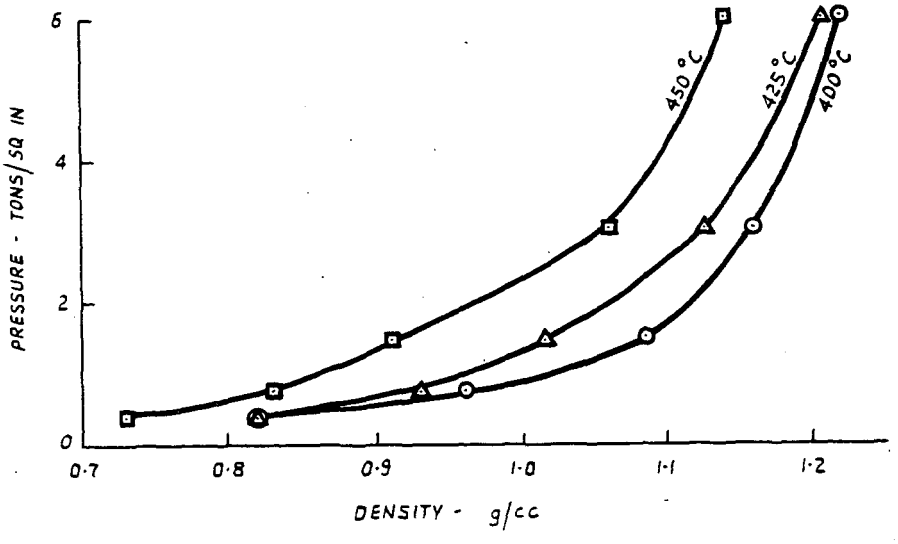


FIG. 6 VARIATION OF COMPACTION WITH PRESSURE.

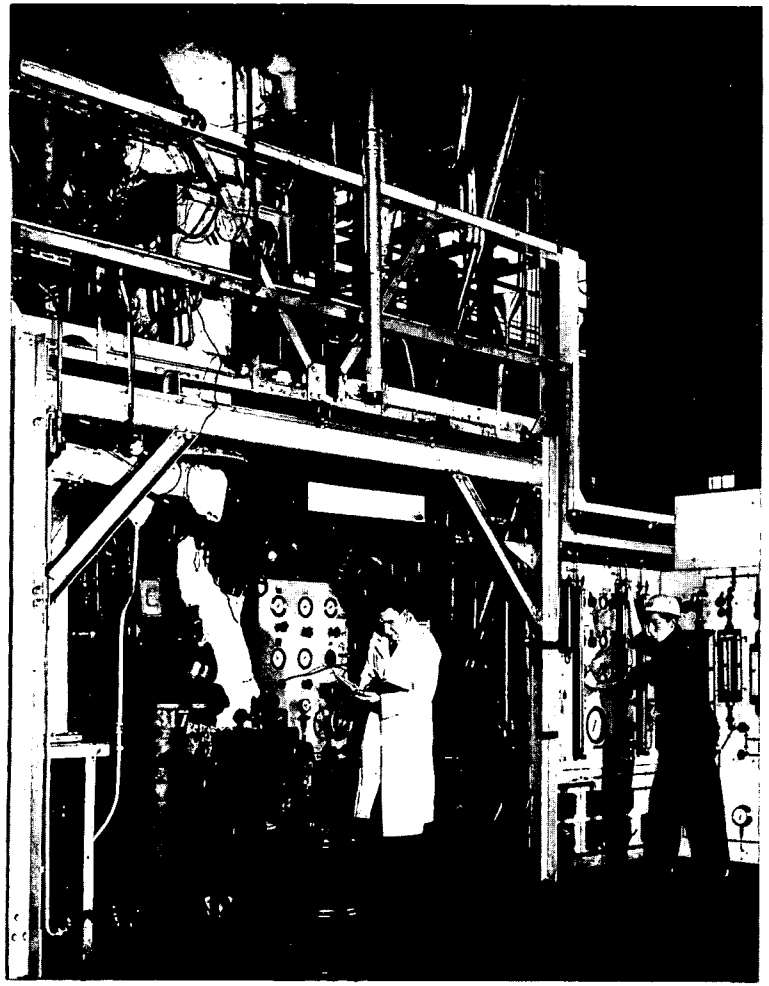


FIG. 7. 100 lb/h PLANT

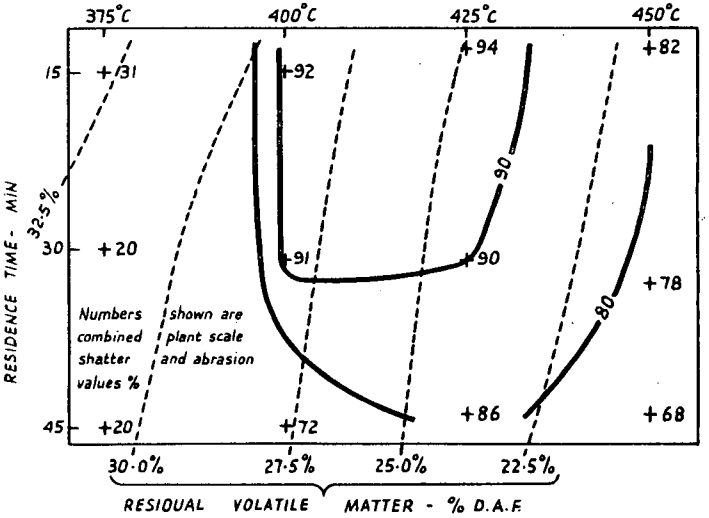
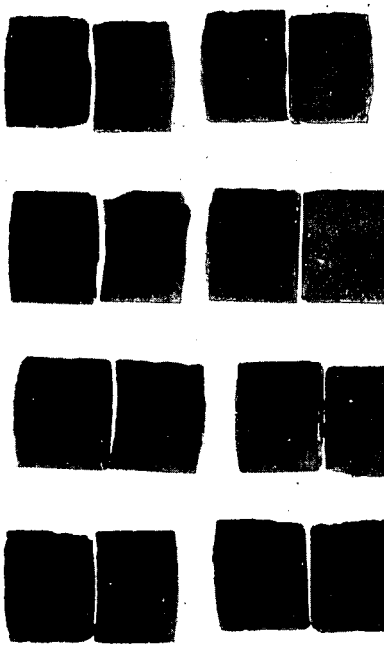


FIG. 8. VARIATION OF STRENGTH WITH TEMPERATURE AND RESIDENCE TIME. (PLANT RESULTS)



Briquettes dry quenched

Briquettes wet quenched after 20 min. dry quenching

Briquettes wet quenched after 10 min. dry quenching

Briquettes wet quenched

FIG. 9. SECTIONS OF BRIQUETTES AFTER QUENCHING

FIG. 10. TWO-STAGE QUENCHING FACILITIES ON A SMALL PILOT PLANT

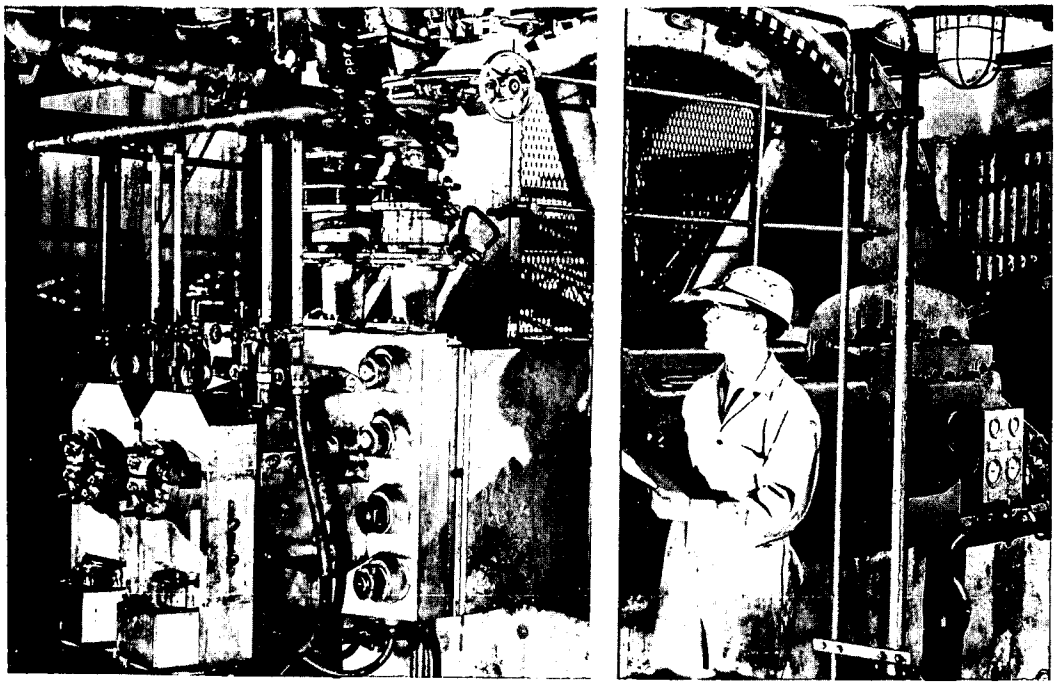


FIG. 11. MECHANICAL EXTRUSION PRESS

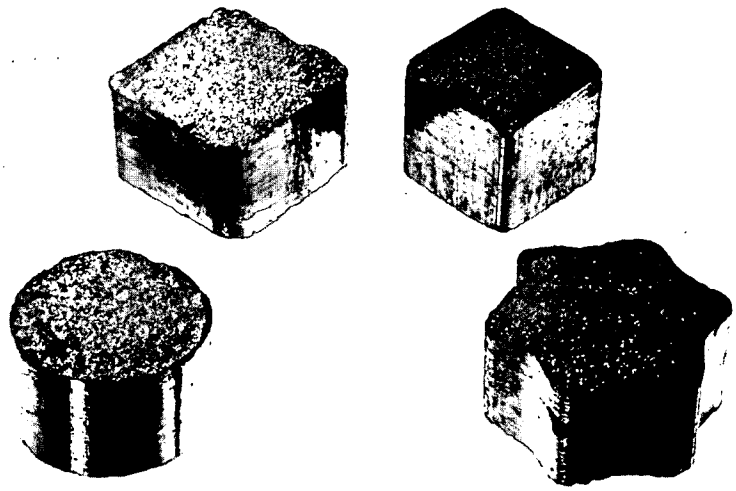


FIG. 12. EXTRUSION BRIQUETTES OF VARIOUS CROSS - SECTION

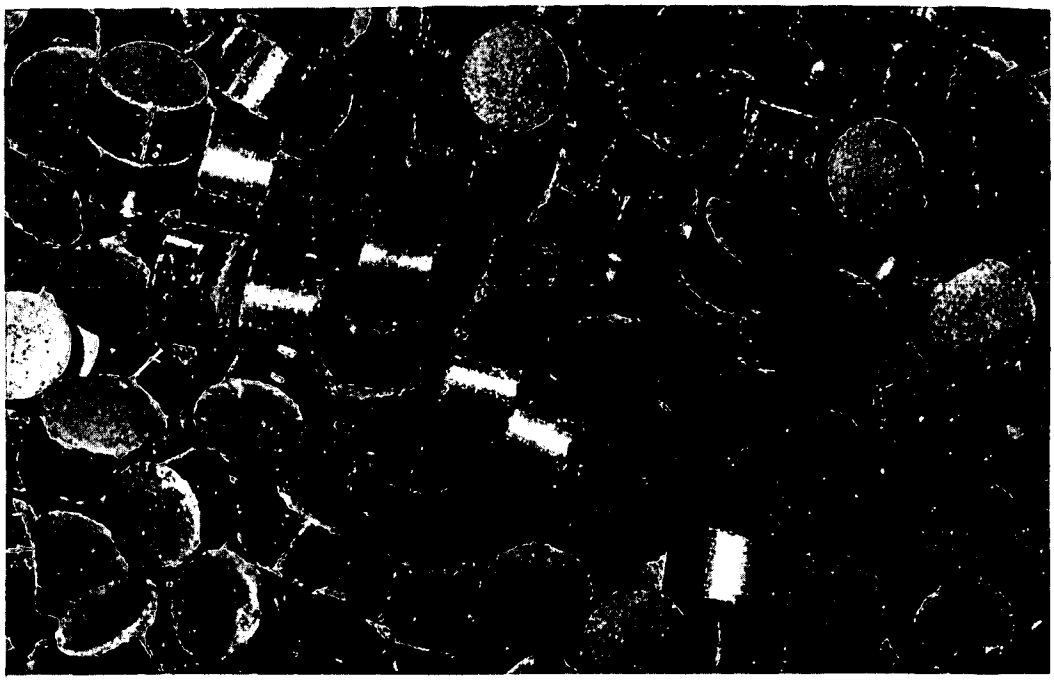


FIG. 13. BRIQUETTE APPEARANCE AFTER 200 MILES RAIL TRANSPORT

THE SLOW OXIDATION OF METHANE. I. A KINETIC STUDY

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Introduction

A number of rate expressions have been proposed for the oxidation of methane based upon measurements of the changes which occur in the total pressure of the reacting gas mixture. Bone and Allum (1) found that the rates of reaction were affected by the initial composition of the mixture. The highest rate under a given set of conditions was obtained when the ratio of the initial pressure of methane to that of oxygen was 2 to 1. This result was confirmed recently by Egerton and his co-workers (2). Norrish and Foord (3) proposed the rate equation:

$$\text{rate}_{max} = \frac{k(CH_4)_o^2(O_2)_o P_o d}{S} \qquad (I)$$

where $(CH_4)_o$, $(O_2)_o$, and P_o are initial pressures of methane, oxygen, and total pressures of methane, oxygen, and total pressure respectively, d is the diameter of the reaction vessel, and S is the surface activity per unit area. Later, Hoare and Walsh (4) suggested the rate expression

$$\text{Max rate} \propto (CH_4)_o^m (O_2)_o^x (P_o)^t e^{-E/RT} \qquad (II)$$

where m, x, and t are reaction orders which vary with the reaction vessel used. The m values ranged from 1.6 to 2.4, the x value from 1.2 to 1.7, and the t values from 0.5 to 0.9.

Recently Egerton and his colleagues (2) and Karmilova *et al* (5) have followed not only the changes in the total pressures but also the changes in the concentrations of reactants, intermediates, and products in each experiment. This was done by repeatedly preparing identical systems and then quenching them at various time intervals; these quenched systems were then analyzed for each component. On the basis of such experiments, Karmilova proposed the expression

$$\frac{d(CH_4)_{max}}{dt} = k(CH_4)_o^{\alpha}(O_2)_o^{\beta} P_o^{\gamma} \qquad (III)$$

where $\frac{d(CH_4)_{max}}{dt}$ represents the rate values ("constant rates") obtained from the slopes of the straight line portion of the rate curves (zero order plots). The values of α, β, and γ were given as 1.62, 0.96, and ≈ 0.1 respectively. The sum of these is approximately 2.7 which agrees well with the value ($n = 2.6$) obtained by Egerton *et al* (2) but which differs from that of Norrish and Foord (3) ($n = 4.0$).

The most recent equation has been proposed by Enikolopyan (6), Semenov (7), Karmilova (8) and their co-workers on the basis of a theoretical treatment of the mechanism of the oxidation:

$$\frac{d(CH_4)_{max}}{dt} = \frac{2k_2k_8}{k_6}\left(\frac{k_2k_5}{k_2'k_5'}\right)^{\frac{1}{2}}(CH_4)^2(O_2) \qquad (IV)$$

In this equation, the k's are rate constants of a series of free radical reactions and (CH_4) and (O_2) are instantaneous partial pressures of methane and oxygen.

Although these authors (8) believed that equation IV is in good agreement with equation III, these equations are not identical. The maximum rate in the former (III) expression is dependent upon the initial partial pressures of methane and oxygen and that in the latter (IV) upon the instantaneous partial pressures of the reactants. Moreover, equation IV does not agree with many of their experimental results. For example, equation IV demands that the rate be second order with respect to methane and first order with respect to oxygen. Yet, the experimental results show that in some cases the rate of methane and oxygen consumption and of carbon monoxide formation is constant up to 50% completion of the reaction (5).

The foregoing resume makes it clear that additional evidence is still needed before the extent of the validity of the previously proposed rate equations and reaction mechanisms for the oxidation of methane can be established. Such evidence is difficult to obtain from the experimental techniques customarily used. Measurements of the changes in total pressure are inadequate for the determination of the reaction order with respect to methane and to oxygen or of the activation energy. Also, while the quenching technique can provide such evidence, it is laborious, time-consuming, and requires a vast number of separate experiments to examine in detail all the parameters in the reaction.

In addition to the experimental limitations of the earlier work, the role of carbon monoxide - the most stable intermediate in the oxidation of methane - has not yet been clarified. Yet, evidence has shown (5) that the oxidation of methane and of carbon monoxide occur simultaneously in the later stages of the reaction. Thus, the rate equation cannot be complete without including an expression for the oxidation of carbon monoxide.

In the present work, the oxidation of methane has been re-examined in detail. The partial pressures of methane, oxygen, and carbon monoxide have been followed by periodic withdrawal and analysis of small samples of the reacting gas mixture by means of gas chromatography. This technique permits a rapid, convenient, and accurate analysis for the separate components throughout each oxidation experiment.

Using this new technique, data have been obtained from which the reaction order with respect to methane and to oxygen can be examined and from which the apparent energies of activation can be calculated. A study has also been made of the methane-initiated oxidation of carbon monoxide.

Experimental

I. Reactants

Research grade methane, 99.54% pure (Phillips Petroleum Co.) was used without further purification. Oxygen, 99.5% pure (Liquid Carbonic, Division of General Dynamics) and carbon monoxide, c.p. grade (Matheson Co.) were dried through a column of 5A molecular sieve material (Fisher Scientific Co.) before use.

II. Apparatus

The apparatus consists of a gas introduction system, reaction vessel, gas sampling system, and a gas chromatograph connected as shown in Figure 1. The gas

chromatograph (Perkin-Elmer Corp. Model 154D) is equipped with a thermistor detector and a 2-meter column packed with molecular sieve material ("Column I").

III. Measurements of Partial Pressures

To measure the partial pressures of each of the gases during the oxidations, it was necessary to establish the relation between the chromatographic peak height and the quantity of each individual gas. For this purpose, gases were introduced through inlets 3 to the sampling capillary 9 located between stopcocks C and D. This capillary, 1 mm I.D. and 70 mm long, contained about 0.08 ml of gas. The pressure of the gas was measured on manometer 2. C and D are 3-way stopcocks with 1 mm. bore and Teflon plugs, while E is a 2-way glass stopcock with 2 mm. bore. By manipulating stopcocks C and D and also E, the gas trapped in the sampling capillary was pushed by the carrier gas, helium, into the gas chromatograph and a corresponding peak appeared on the recorder chart. The peak heights were plotted as a function of the pressures of the gases as shown in Figure 2. Thus for a given condition, $P = aH$ where P is the gas pressure, H is the peak height, and a is the proportionality constant. The value of a varies with the pre-set conditions, such as column temperature, flow rate of carrier gas, and volume of sampling capillary. In addition, repeated use of the chromatographic column may also change a. In the work reported here, the value of a for each individual gas was re-ascertained before each oxidation experiment.

IV. Oxidation Experiments

For the oxidation experiments, the separate gases were admitted through inlets 3 to the individual gas burets 5. The desired amounts (approx.) of the components of the reaction mixture were then pumped from the gas burets into the reaction vessel 7 using pump 6. The cylindrical reaction vessel was constructed of borosilicate glass (30 mm. I.D. with a volume of 100 ml.) and contained a thermocouple well along its longitudinal axis. In some experiments as indicated below, the vessel was used without further treatment and in others, it was first treated with hydrofluoric acid; for this treatment, the vessel was shaken with 20-25% hydrofluoric acid in water, then washed exhaustively with distilled water, and dried at 400°C at less than 1 mm. of Hg.

During the course of the oxidation experiments, the reaction vessel was maintained at the desired operating temperatures ±1°C by the thermocouple, temperature controller (Wheelco), variable transformer and furnace 8.

To determine the composition of the gases in the vessel at the start and during the experiments, a large fraction (ca. 55%) of the gas mixture was withdrawn from the reaction vessel and passed through the sampling capillary by lowering the mercury level in the modified 125 ml Toepler pump 11. Raising the level returned the gas through the capillary to the vessel. Two cycles were needed before each sampling in order to obtain reproducible analyses; each cycle required only about 15 seconds. The small sample of gas (0.08 ml) was then pushed into the gas chromatograph with helium as described above. In such manipulations, some helium was inevitably introduced into the reaction vessel during sampling but it appeared to have no effect upon any of the reactions studied.

Results and Discussion

In many of the experiments reported earlier, carbon monoxide accumulated in much larger amounts than any other reaction intermediates, such as formaldehyde or hydroperoxide. In addition, Karmilova et al (9) were able to show by tracer techniques that the carbon dioxide formed in the oxidation of methane was produced almost

exclusively from the oxidation of carbon monoxide. Thus, although the less stable intermediates may contribute to the mechanism, the kinetics of the overall oxidation can be examined in terms of the stepwise reactions represented by equation V and VI.

$$CH_4 + 3/2\ O_2 \rightarrow CO + 2H_2O \qquad (V)$$

$$CO + 1/2\ O_2 \rightarrow CO_2 \qquad (VI)$$

I. The Oxidation of Methane to Carbon Monoxide (eq. V)

A. The reaction order with respect to methane and oxygen. To minimize the effect of carbon monoxide on the reaction kinetics, the ratio of the initial pressures of methane, $P^o_{CH_4}$, to that of oxygen, P_{O_2}, was increased in some experiments. When the ratio is about 3 or higher, the reaction is zero order with respect to oxygen and to methane; the results of typical experiments with both untreated and HF-treated vessels are shown in Figure 3. With such high ratios, the rates of consumption of methane and oxygen and the rates of accumulation of carbon monoxide are constant up to 90% completion of the reaction. These rates can be expressed as:

$$-\frac{dP_{O_2}}{dt} = k_1 \qquad (VII)$$

$$-\frac{dP_{CH_4}}{dt} = \frac{dP_{CO}}{dt} = 2/3\ k_1 \qquad (VIII)$$

where k_1 is the zero order rate constant.

When the ratio of $P^o_{CH_4}$ to $P^o_{O_2}$ is reduced to unity or less, the rates are constant only up to about 30 to 70% completion. In these experiments, sufficient carbon monoxide accumulates so that it is oxidized competitively with methane. The rate equations (VII and VIII) can no longer be applied for the whole reaction but only for the initial stage where the rates are constant (Figure 4).

These constant rates have been observed by all previous investigators but have been generally identified by them only as "maximum rates" (equations I, II, and III). They were interpreted differently by previous investigators. Semenov (7, 10) has suggested that the oxidation of methane is a free radical chain degenerating process in which the formation of formaldehyde is the slow step of the reaction and the steady state of formaldehyde results in a constant rate. This interpretation has been accepted by many previous investigators. Recently, however, Karmilova et al (11) found that the rate remains constant even when the concentration of formaldehyde undergoes a marked decrease and, therefore, the postulation of the steady state concentration of formaldehyde as a controlling feature of the reaction is untenable. To explain these constant rates, they proposed that the oxidation of methane undergoes additional catalysis by one of the reaction products formed after formaldehyde. The observed constant rate may then result from a superposition of the rates of two autocatalytic processes, the increase in the rate of one due to oxidation of methane being compensated by the decrease in the rate of the other. They suggested several possible additional catalysts, such as hydrogen peroxide, hydroxy radical, etc. No evidence was given to support this view.

B. The effect of initial pressures of methane and oxygen. The results for the effect of $P^o_{CH_4}$ and $P^o_{O_2}$ on the value of k_1 are shown in Tables 1 and 2. In general,

k_1 increases with increasing either $P^0_{CH_4}$ or $P^0_{O_2}$, or both. $P^0_{CH_4}$ has more effect upon k_1 than does $P^0_{O_2}$. An empirical equation is proposed to account for the dependency of k_1 on the initial pressures:

$$k_1 = k_1' \frac{P^{0^2}_{CH_4} P^0_{O_2}}{P^0_{CH_4} + P^0_{O_2}} \qquad (IX)$$

where k_1' is a pressure independent rate constant. The values of k_1' are listed in Column 5 of Table 1 and Column 6 of Table 2. The validity of equation IX is indicated by the linear relationship in the plot of k_1 vs $\frac{P^{0^2}_{CH_4} P^0_{O_2}}{P^0_{CH_4} + P^0_{O_2}}$ for the reactions at different temperatures in an HF-treated vessel as shown in Fig. 5. For the reaction in an untreated vessel, k_1 at 399°C increases linearly with $\frac{P^{0^2}_{CH_4} P^0_{O_2}}{P^0_{CH_4} + P^0_{O_2}}$ until it appears to reach a limiting value of about 0.17 mm, min^{-1} (Figure 6).

The increase in the maximum rates ("constant rates") as the initial partial pressures increase - observed in this as well as in earlier work (equations I, II and III) - is not accounted for by equation IV which is based on a free radical chain reaction mechanism.

The apparent energy of activation for the oxidation of methane calculated from k_1' values at four different temperatures (Figure 7) is 36.2 kcal/mole. This value differs from the values [43 (5, 6), 60.8 (12), and 61.5 (13)] obtained by earlier workers from the maximum rates.

C. The induction period. For the reactions below 455°C, an induction period has been observed which ranges from 1 min. to 350 min. as shown in Tables 1 and 2. The initial pressures of methane and oxygen affected this induction period but the exact relationship remains to be established. In general, the reactions in the untreated vessel had longer induction periods than those in the HF-treated vessel. It was noted that the induction period was extremely long when an untreated vessel was used for the first time. Also, the induction period is longer for reactions at lower temperatures than those at high temperatures. At 482°C and above with an HF-treated vessel, the induction period is negligible.

II. Methane-Initiated Oxidation of Carbon Monoxide (Equation VI)

In the course of the oxidation of methane when the ratio of the partial pressure of carbon monoxide to methane becomes appreciable, then the rate of disappearance of methane no longer follows the zero order equation (eq. V). Additional attention must therefore be devoted to the oxidation of carbon monoxide and to the role it plays in the oxidation of methane.

The oxidation of carbon monoxide itself requires temperatures of about 1000°C (14); however, in the presence of water vapor, this temperature may be lowered to about 400°C (15). There is no doubt that methane can also initiate the oxidation of carbon monoxide (15). A detailed study of this reaction is presented below.

A. Reaction in the presence of water. Since water can also initiate the oxidation of carbon monoxide, a comparison was made between the effect of methane and that of water. As shown in Fig. 8, when the mixture of carbon monoxide, oxygen and water vapor was heated at 427°C in an HF-treated vessel, the oxidation was slow. It became fast after methane was introduced.

B. Reaction order with respect to carbon monoxide and oxygen. In these experiments, dried carbon monoxide and oxygen were introduced into the HF-treated vessel at various temperatures ranging from 427° to 516°C. The reactions were extremely slow. However, the rate of reaction increased rapidly when a small amount of methane was introduced. The results of one such experiment are shown in Fig. 9. In all the present results, the methane-initiated oxidation of carbon monoxide is a second order reaction, first order with respect to carbon monoxide and to oxygen. The rate can be expressed as:

$$-\frac{dCO}{dt} = k_2 P_{O_2} P_{CO} \qquad (X)$$

where k_2 is the second order rate constant. The temperature dependence of k_2 (Fig. 7 and Table 3) leads to an apparent activation energy of 60.7 kcal/mole.

As shown in Fig. 9, the linear relationship of the second order plot was maintained despite the decrease in pressure of methane from 13 mm to almost zero during the course of the reaction. This was observed in every experiment on the methane-initiated oxidation of carbon monoxide. k_2 does not depend, therefore, upon the instantaneous pressure of methane. Instead, there appears to be some relationship (Table 4) between k_2 and the initial pressure of methane - analogous to that exhibited by k_1 - although no satisfactory correlation has yet been obtained.

In another type of experiment (Fig. 10), additional carbon monoxide was added to a reacting mixture of methane and oxygen (and carbon monoxide produced) when the methane had decreased to 3.2 mm. A linear relationship was again obtained for the second order plot of $\log \frac{2P_{O_2}' - P_x}{P_{CO}}$ versus time t. In this expression, P_{O_2}' is the pressure of oxygen at the time when carbon monoxide was introduced, P_x is the pressure of carbon dioxide produced after that time, and P_{CO} is the instantaneous pressure of carbon monoxide. In this experiment k_1, 8.9 mm, min^{-1}, was determined from the initial rate of consumption of oxygen and k_2, 8.2×10^{-6} mm^{-1}, mm^{-1}, was obtained from the slope of the second order plot. This value of k_2 agrees well with those of Table 3 and once again appears to be related to the initial pressure of methane. If it depended upon the instantaneous pressure of methane when the carbon monoxide was added, viz. 3.2 mm, k_2 should be below 2.6×10^{-6} mm^{-1}, mm^{-1} (Table 4).

III. Nature of the Oxidative Process

In the present work, during each sampling procedure, about 55% of the gas mixture was withdrawn from the reaction vessel to the Toepler pump at room temperature for about 15 seconds and then returned to the vessel. In the second cycle, this was repeated so that more than 80% of the reaction mixture may have been quenched during

each sampling. Even in the experiments which had relatively long induction periods, the sampling procedure had no discernible effects upon the rate curves. Therefore, it appears that the oxidation of methane must be a heterogeneous reaction inasmuch as quenching would affect the kinetics of a homogeneous reaction. Also, the apparent energy of activation for the oxidation of methane is 36.2 kcal/mole whereas that of carbon monoxide is much higher, i.e., 60.7 kcal/mole. It is difficult on the assumption of a homogeneous reaction to reconcile this wide disparity in energies of activation with the observations that both gases oxidize competitively during the reaction. Likewise, the rate of oxidation of methane depends upon the initial pressures of methane and oxygen rather than upon the instantaneous pressures as would be expected for a homogeneous reaction.

Some consideration of the possible nature of the heterogeneous process is warranted. On the basis of the present results, it appears that methane and oxygen react initially to form certain active sites or intermediate complexes on the surface of the reaction vessel. These active sites in turn can catalyze the oxidation of both methane and carbon monoxide which are zero order and second order reactions, respectively. The activity of these sites per unit area depends upon the initial concentrations and remains constant throughout the reaction. As the oxidation proceeds, carbon monoxide is produced in the reaction. This product in turn competes with the methane for the same active sites. A similar suggestion has been made by Von Meersche (16). As the concentration of the carbon monoxide becomes significant with respect to that of methane, then the consumption of methane deviates from the zero order rate. If the methane and carbon monoxide did not compete for the active sites but instead competed for the remaining oxygen, then the zero order rate for the consumption of methane should remain constant throughout the reaction. However, this has not been observed.

The detailed mechanism of this reaction and the nature of the active sites remain to be studied.

Summary

1. A stepwise oxidation of methane to carbon monoxide and then to carbon dioxide is demonstrated. The oxidation of methane to carbon monoxide is a zero order reaction with respect to both methane and oxygen. The zero order rate constant is dependent upon the initial pressures of both methane and oxygen. The correlation of this constant with initial pressures is indicated by an empirical equation. The apparent energy of activation for this reaction was calculated to be 36.2 kcal/mole.

2. The reaction in an untreated vessel has a longer induction period and slower rate than that in an HF-treated vessel.

3. The oxidation of carbon monoxide is initiated by methane or its oxidation product and is a second order reaction, first order with respect to oxygen and to carbon monoxide. The second order rate constant appears to vary with the initial pressure of methane. The apparent energy of activation for this reaction is 60.7 kcal/mole.

4. The oxidation of methane appears to be a heterogeneous process. It is suggested that during the induction period, methane and oxygen react to form active sites or intermediate complexes on the surface of the reaction vessel. Methane and its oxidation product, carbon monoxide, then compete for these sites rather than for oxygen.

Acknowledgment

The author is indebted to Dr. C. H. Ruof for his encouragement and guidance in the course of this work.

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Table 1 - Oxidation of Methane in an HF-Treated Vessel at Various Temperatures

Expt. No.	T°C	$P^o_{O_2}$, mm	$P^o_{CH_4}$, mm	k_1, mm, min.$^{-1}$	$k_1' \times 10^5$, mm^{-1}, min.$^{-1}$	Induction Period, min.
32	399	127	317	1.5	5.22	40
33	"	83.4	364	1.44	5.83	35
34	"	380	330	3.02	5.18	16
35	"	378	148	0.89	5.65	20
36	427	399	151	2.82	17.1	14
37	"	151	344	6.5	18.0	5
38	"	154	126	1.7	19.5	10
39	"	154	346	5.64	15.3	4
40	"	372	364	11.7	17.5	5
41	454	347	161	8.0	45.2	3
42	"	185	355	18.2	42.2	1
43	"	115	106	2.55	43.4	3
44	"	204	187	8.9	48.9	3
45	"	265	234	16.6	57.1	3
46	"	312	306	23.2	49.1	4
47	"	308	371	33.0	52.9	4
24	482	383	306	47.5	86.4	< 1
25	"	209	298	32.0	87.4	"
26	"	122	308	23.1	86.2	"
27	"	278	267	37.5	101	"
28	"	196	272	32.5	105	"
29	"	186	107	6.5	89.4	"
30	"	112	342	28.3	98.1	"
31	"	111	346	24.3	83.6	"

Table 2 - Oxidation of Methane in an Untreated Vessel at 399°C

Expt. No.	$P^o_{O_2}$, mm	$P^o_{CH_4}$, mm	k_1, mm, min.$^{-1}$	k_1', mm^{-1}, min.$^{-1}$	Induction Period, min.
2*	79	408	0.13	4.8×10^{-6}	350
3	96.4	306	0.17	7.0×10^{-6}	55
4	226	288	0.17	4.7×10^{-6}	50
5	151	265	0.16	6.3×10^{-6}	48
6	83.6	273	0.15	8.6×10^{-6}	56
7	39	372	0.15	11.4×10^{-6}	40
8	74	311	0.16	8.6×10^{-6}	50
9	243	111	0.042	5.0×10^{-6}	150
10	220	71.4	0.043	11.2×10^{-6}	60
11	236	156	0.17	12.0×10^{-6}	40
12	280	94	0.06	9.0×10^{-6}	40
13	287	95.5	0.033	8.6×10^{-6}	50
14	179	75	0.05	12.7×10^{-6}	120
15	246	120	0.06	6.2×10^{-6}	150

*E2 was in a new vessel used for the first time.

Table 3 - Dependency of k_2 on Temperature

Expt. No.	$P^o_{CH_4}$, mm	T°C	k_2, mm^{-1}, min^{-1}
E104	13.0	516	1.70×10^{-4}
E98	12.5	516	1.20×10^{-4}
E103	13.5	504	7.36×10^{-5}
E99	14.0	482	2.27×10^{-5}
E102	13.4	482	3.125×10^{-5}
E101	11.0	454	5.5×10^{-6}

Table 4 - Dependency of k_2 on $P^o_{CH_4}$ (482°C)

Expt. No.	$P^o_{CH_4}$	k_2
118	3.7 mm	2.6×10^{-5} mm^{-1}, min^{-1}
116	8.1	4.8×10^{-5}
117	14.9	5.0×10^{-5}
115	19.7	6.7×10^{-5}

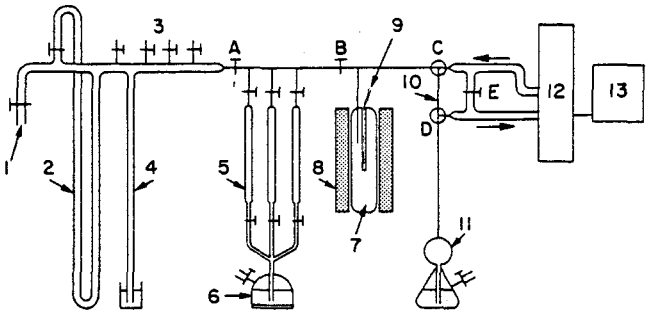

Fig. 1. - Reaction system. 1. Vacuum inlet; 2. Manometer; 3. Gas inlet; 4. Pressure relief device; Gas burets; 6. Mercury pump; 7. Reaction vessel (100 ml.); 8. Furnace; 9. Thermocouple; 10. Sampling capillary; 11. Toepler pump (125 ml.); 12. Gas chromatograph; 13. Recorder.

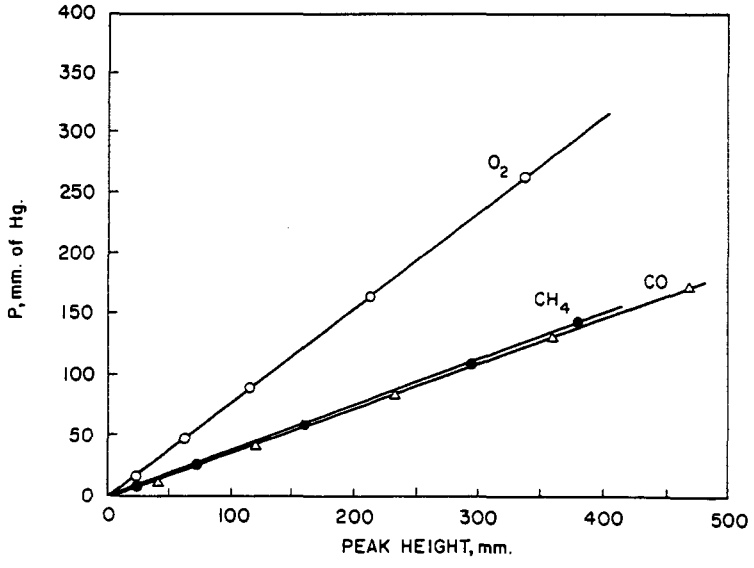

Fig. 2. - Calibration of peak heights against pressures.

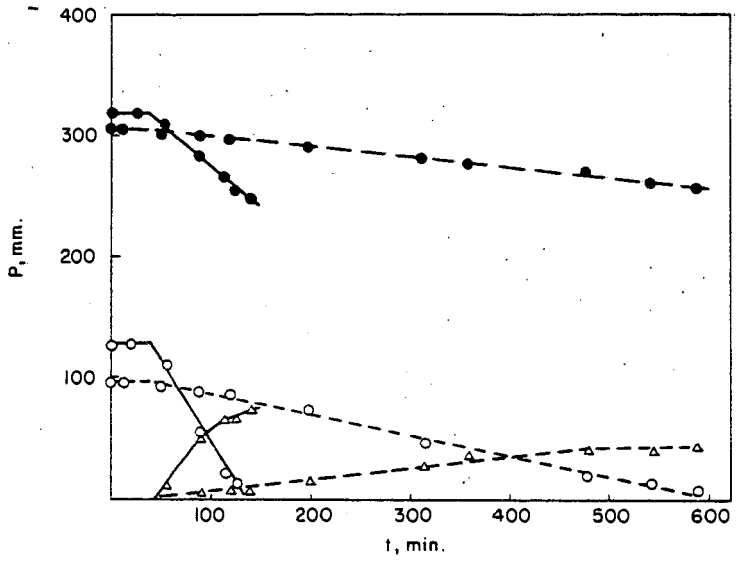

Fig. 3. - Rate curves for the oxidations of methane at 399° C. ○, O_2; ●, CH_4; △, CO. Broken lines, untreated vessel (E3); solid lines, HF-treated vessel (E32).

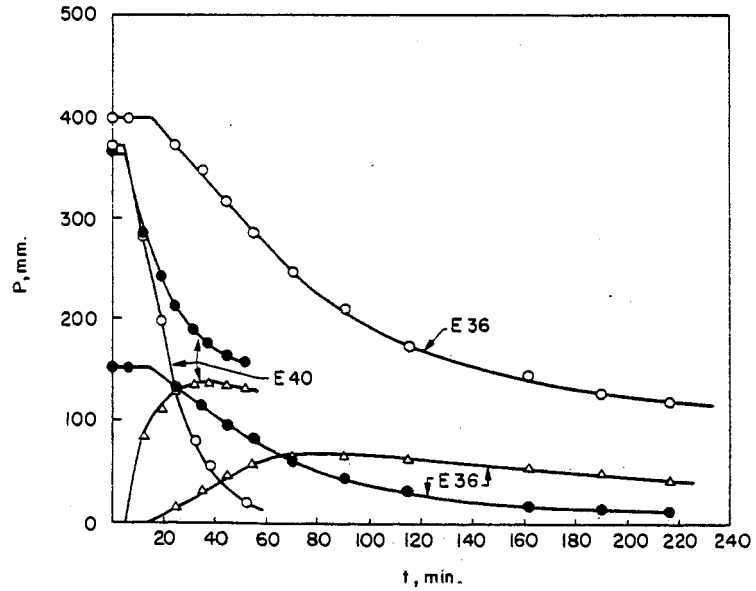

Fig. 4. - Rate curves for the oxidations of methane in HF-treated vessel at 427° C. Experiment 36, $P^{o}_{CH_4}/P^{o}_{O_2} = 0.38$; Experiment 40, $P^{o}_{CH_4}/P^{o}_{O_2} = 0.98$. ○, O_2; ●, CH_4; △, CO.

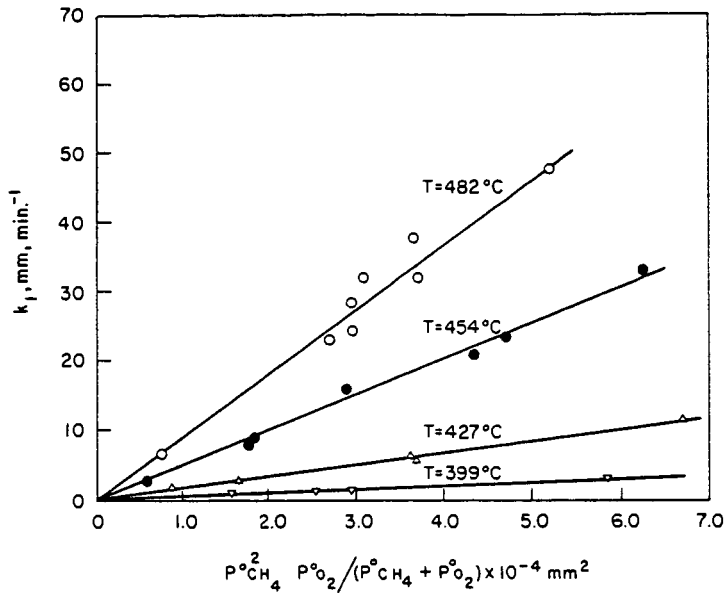

Fig. 5. - Dependence of k_1 on initial pressures of methane and oxygen (oxidations in HF-treated vessel).

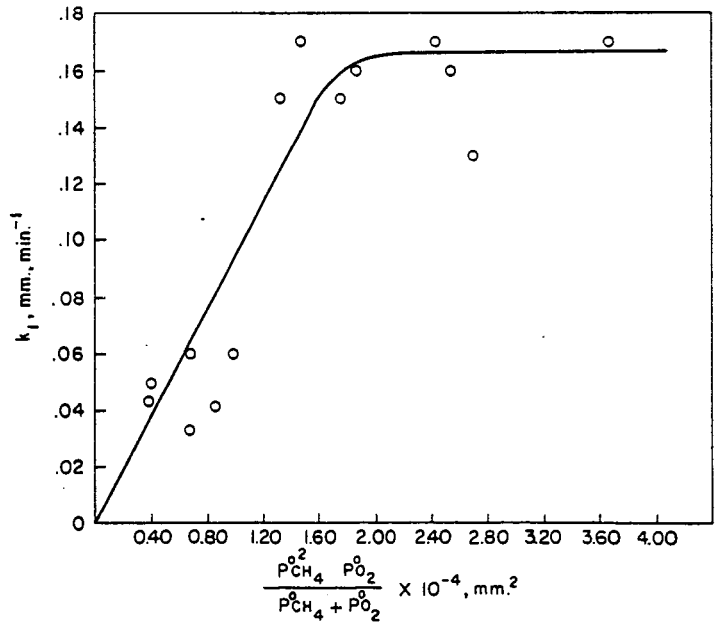

Fig. 6. - Dependence of k_1 on initial pressures (oxidations in untreated vessel at 399° C).

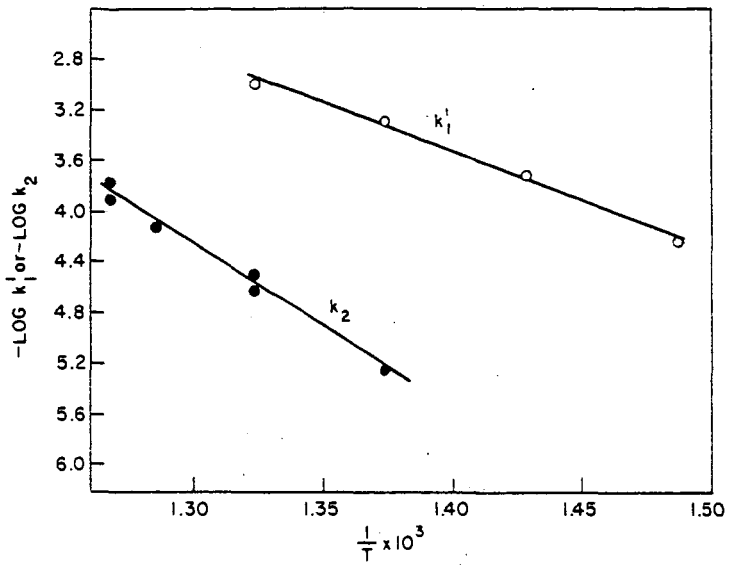

Fig. 7. - Arrhenius plot for the determination of the apparent activation energy.

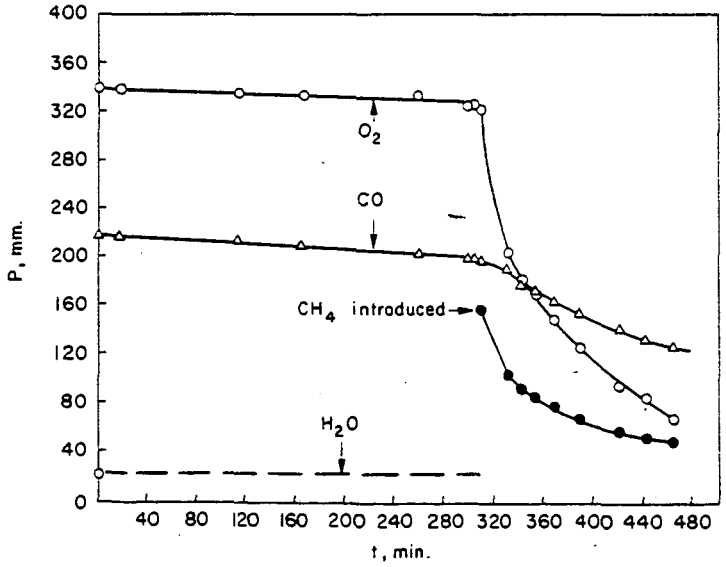

Fig. 8. - Oxidation of carbon monoxide in the presence of water (22 mm. of Hg) and methane at 427° C (E60).

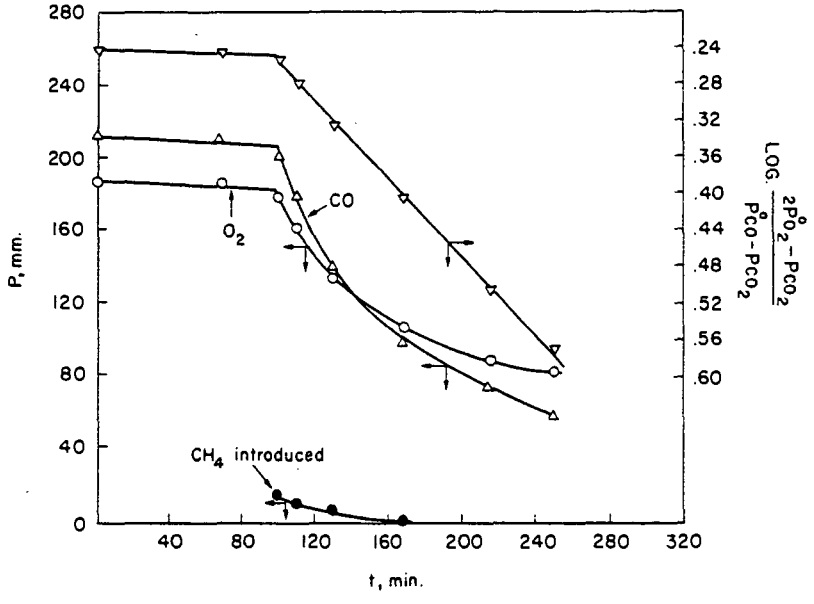

Fig. 9. - Rate curves for the methane-initiated oxidation of carbon monoxide at 504° C.

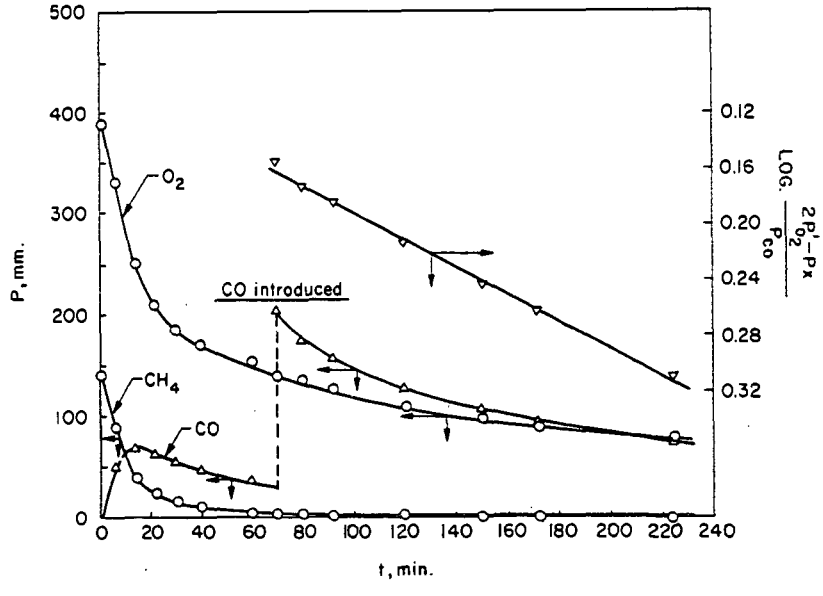

Fig. 10. - Determination of k_1 and k_2 in the oxidation of methane.

New Developments in Catalysts for Producing a High-B.t.u. Gas via the Hot Gas Recycle Process

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INTRODUCTION

A high-B.t.u. gas can be produced from coal by gasifying the coal to make H_2+CO, and then reacting these gases, after purification, over a catalyst to make a gas consisting essentially of methane. (A satisfactory high-B.t.u. gas would have a minimum calorific value of 900 B.t.u. per cubic foot and a maximum carbon monoxide content of 0.1 percent.) A methanation process under development in the Federal Bureau of Mines at Bruceton, Pa., at the present time is the hot-gas-recycle process.

In the hot-gas-recycle system the exothermic heat of reaction (about 280 B.t.u. per cubic foot of methane produced) is absorbed by the sensible heating of large volumes of recycle gas circulating through the reactor in direct contact with the catalyst. Because of the large volumes of gas and the high cost of compression, it is necessary to have a low pressure drop through the catalyst bed. The development by the Bureau of an active, durable catalyst made of steel lathe turnings that pack with a high void volume and offer little resistance to flow made the hot gas recycle feasible.

This paper describes methanation in two stages using a steel lathe turning catalyst in the first reactor and nickel catalyst in the second to complete the conversion of synthesis gas. By this method the amount of nickel catalyst needed is considerably less than that usually required in methanation processes. Previous results have been reported for use of granular Raney nickel as catalyst in the second reactor.[1/] In this paper pilot plant results are shown comparing operation of the second reactor with granular catalysts and with nickel catalysts in the form of plates either of solid Raney nickel or nickel sprayed on steel or aluminum. These latter materials offer a negligible flow resistance and permit efficient use of a small amount of expensive nickel catalyst.

Table 1 shows the principal reactions occurring in the synthesis. Equations 1 and 2 are the synthesis reactions for the formation of hydrocarbons. Equation 3 is the water gas shift reaction. Equation 4 is an undesirable carbon deposition reaction, and 5 the carbide reaction. All these reactions are exothermic at synthesis temperature of 300° C.

TABLE 1. Reactions occurring in hot-gas-recycle process

1.	$3H_2 + CO$	$\rightleftharpoons$	$CH_4 + H_2O$
2.	$2nH_2 + nCO$	$\rightleftharpoons$	$(CH_2)_n + nH_2O$
3.	$H_2O + CO$	$\rightleftharpoons$	$CO_2 + H_2$
4.	$2CO$	$\rightleftharpoons$	$CO_2 + C$
5.	$2CO + 2Fe$	$\rightleftharpoons$	$CO_2 + Fe_2C$

EXPERIMENTAL PROCEDURE AND RESULTS

A flowsheet of the hot gas recycle process is shown in figure 1. Two reactors are used in series, the first, using steel lathe turnings, converts 70-90 percent of the synthesis gas, and the second, using nickel, converts essentially the remainder. The total feed gas passes down through the first reactor, then through a cyclone trap and is divided. Part flows to the second reactor; the remainder is recompressed to 425 p.s.i.g. and recycled to the reactor, 90 to 95 percent as hot recycle and the balance as cold recycle. As water is condensed and removed from the cold recycle, the amount of cold recycle is used to control the water vapor content of the total recycle gas. The synthesis gas then combines with the recycle gas and flows to the main reactor.

The tail gas flows to the second reactor which is operated at a lower recycle rate. In the absence of a hot-gas compressor, it was necessary to cool the whole recycle stream. The product stream is depressurized, metered, and analyzed.

Table 2 shows the results of typical tests operating with $3H_2+1CO$ feed gas using one or two reactors. The first column shows results achieved using only one reactor which contained steel turnings as catalyst. The turnings had been oxidized with steam and reduced with hydrogen to produce an active catalytic surface. The calorific value of the product gas was 720 B.t.u. per cubic foot. The carbon monoxide content was 2.1 percent. The methane content was 31.9 percent with significant quantities of ethane and propane. The feed-gas conversion was 83.4 percent. The second column of the table shows results obtained with both reactors operated in series. The second reactor contained Raney nickel of 4-20 mesh size. The heating value of the product gas increased to 986 B.t.u. per cubic foot, and the carbon monoxide content decreased to 0.1 percent. The methane content was 93.5 percent. In addition to methanating the carbon monoxide, most of the carbon dioxide reacted and the heavier hydrocarbons cracked and were hydrogenated to methane.

Because the Raney nickel catalyst used in the second reactor was in the form of granules, the pressure drop across the second reactor was higher than desired for hot-gas-recycle operation. Raney nickel is too brittle to be machined to lathe turnings, the physical form used for the catalyst in the first reactor. To overcome this difficulty, two types of nickel catalyst plates were devised. Plates were sawed from an ingot of Raney nickel and assembled in a parallel array to fit into the 3-inch diameter reactor as shown in figure 2. Plates were 5-3/4 inches high and 1/8 inch thick. A second type consisted of assemblies made of steel or aluminum plates sprayed with Raney nickel powder or nickel oxide powder using a oxy-hydrogen or oxy-acetylene torch. The powder of 100-300 mesh size was sprayed on 1/16-inch plates to a thickness of 0.040-0.060 inch on each side and edge. An average of 350 grams of Raney nickel or 250 grams of nickel oxide was on the surface of each assembly.

TABLE 2. Synthesis results using one or two reactors,[a] steel turnings in first reactor, granular Raney nickel in second

Reactors	1	2
Space velocity to first reactor, vol. of gas/vol. of catalyst/hour	850	850
Space velocity to second reactor	---	10,000
Exit gas analysis (vol.-percent-dry basis)		
H_2	48.6	2.8
CO	2.1	0.1
N_2	0.5	.8
CO_2	6.8	1.4
C_1	31.9	93.5
$C_2=$	0	0
C_2	5.4	0.9
$C_3=$	0.2	.1
C_3	2.9	.3
C_4+	1.6	.1
Heating value, B.t.u./cu. ft.	720	986
H_2+CO conversion, percent	83.4	99.3
Avg. temperature, °C. 1st reactor	320	319
Avg. temperature, °C. 2nd reactor	---	321

[a] $3H_2$+1CO feed to the first reactor.

The plate assemblies sprayed with Raney nickel were activated by digesting with a 3-percent NaOH solution to remove 20 percent of the aluminum. Those sprayed with nickel oxide were activated by reducing with hydrogen. The nickel oxide was a sinter material of the composition shown in table 3.

TABLE 3. Analysis of Raney nickel and nickel oxide[a]

Material	Raney nickel	Nickel oxide
Nickel	42-40	74.2
Aluminum	58-60	
Cobalt		1.04
Iron		1.94
Copper		0.73
Sulfur		.13

[a] Weight percent.

With the steel turnings being used as a catalyst in the first reactor, consecutive tests were made using solid Raney nickel plates, stainless steel plates sprayed with Raney nickel, and aluminum plates sprayed with nickel oxide sinter in the second reactor. At comparable conditions the pressure drop was reduced about 90 percent, from 17 inches with granular Raney nickel, to less than 2 inches of water per foot of catalyst height, with plates.

Table 4 shows other results of these tests. Except for the carbon monoxide content, a satisfactory high-B.t.u. gas was produced. No significant difference in catalyst activity or product composition was observed with these three catalysts in the second reactor. Since the nickel oxide sinter is as satisfactory as the Raney nickel as a catalyst for the second reactor, it would be preferred as it costs only one-third as much per weight of nickel.

TABLE 4. Results of tests using plate assemblies in second reactor[a/]

	First reactor	Second reactor		
Catalyst	steel turnings	Solid Raney plates	Raney nickel sprayed plates	Nickel oxide sprayed plates
Space velocity, vol./vol./hr.	700	6000	5800	5700
Avg. reactor temp., °C.	321	332	334	329
H_2+CO conversion, percent	73.8	97.3	98.0	97.5
Exit gas analysis, (vol.-percent-dry basis)				
H_2	56.7	9.0	7.5	9.0
CO	4.0	1.8	0.8	0.8
N_2	1.1	0.7	.8	.9
CO_2	8.7	2.4	2.1	2.6
CH_4	23.6	84.5	87.2	85.1
C_2=	0	0	0	0
C_2	3.5	1.0	1.0	1.1
C_3=	0.1	0.1	0.3	0
C_3-	1.7	.4	.3	.4
C_4=	0	0	0	0
C_4+	.6	.1	0	.1
Heating value, B.t.u./cu.ft.	566	925	943	927

a/ $3H_2$+1CO feed to the first reactor.

An advantage of the flame-spraying technique is evident with the nickel oxide. Nickel oxide granules disintegrated to powder on reduction with hydrogen at 400° C. Although the material was active catalytically, it had no mechanical strength. However, the nickel oxide sprayed on plates adhered firmly to the base metal after reduction. Thermal spraying may be applicable to other catalysts which are catalytically active but structurally weak.

Because the plates operated satisfactorily in the second reactor, a few tests were made using them in the first reactor. Table 5 shows the results of these tests. The solid plates of Raney nickel made a product gas with a heating value of 941 B.t.u. per cubic foot. The use of plates sprayed with Raney nickel resulted in gas with a heating value of 877 B.t.u. per cubic foot and the plates sprayed with nickel oxide, 856. In all cases the carbon monoxide content exceeded 0.1 percent. The plates sprayed with Raney nickel were operated at an average temperature of 255° C. When the temperature was raised to over 300° C. they became inactive.

TABLE 5. Results of tests using plate assemblies in first reactor[a/]

Catalyst	Solid Raney nickel plates	Raney nickel on stainless steel plates	NiO on aluminum or stainless steel plates
Space velocity, vol./vol./hr.	1250	1500	3000
Avg. reactor temperature, °C.	347	255	393
H_2+CO conversion, percent	99.0	93.1	95.4
Exit gas analysis (vol.-percent-dry basis)			
H_2	4.2	22.6	14.5
CO	0.3	4.3	1.7
N_2	1.3	0.4	1.2
CO_2	2.7	0.2	3.3
CH_4	91.4	63.5	79.3
C_2=	0	0	0
C_2	0.1	4.5	0
C_3=	0	0.1	0
C_3	0	1.7	0
C_4=	0	0.1	0
C_4+	0	0.7	0
Heating value, B.t.u./cu.ft.	941	877	856

a/ $3H_2$+1CO feed gas.

DISCUSSION

At an hourly space velocity of 6,000 and 330° C., sprayed nickel and solid Raney nickel plates produced a gas with the desired calorific value when used in the second stage of the hot gas recycle pilot plant. However, at this space velocity carbon monoxide values of 0.8 to 1.8 percent were too high. When used as a catalyst in the first reactor, at an hourly space velocity of 1,250 and 347° C., the solid Raney nickel plates produced a product gas of 941 B.t.u. per cubic foot and a carbon monoxide content of 0.3 percent, whereas the sprayed sections in the first reactor produced a gas that was unsatisfactory in both respects, calorific value and carbon monoxide content.

This difference in results between the solid Raney nickel plate assemblies and the plates sprayed with Raney nickel may be due to several factors: 1) The coating may have been too thin and the digestion procedure did not activate sufficient nickel; 2) the coating did not adhere to some of the plates, indicating either faulty sand blasting or spraying technique.

These nickel sections have advantages over steel lathe turnings. Higher conversions and higher heating value gas can be achieved in the first reactor; they can be operated at temperatures as high as 450° C. without significant carbon deposition; they are less susceptible to oxidation by steam, which means that the water vapor content of the recycle gas can be greater (less cold recycle gas). The pressure drop is less than with steel turnings, and because a greater temperature differential can be tolerated, a lower recycle flow is required. This decreases the cost of recompressing the recycle gas considerably. Other factors to be determined are the relative lives of the nickel and steel catalysts and their selective sensitivities to sulfur poisoning.

Other materials such as magnetite ore, fused iron oxide, and cobalt oxide have been sprayed on steel sections and tested in bench-scale units, but none were as active as the materials discussed.

CONCLUSIONS

While a good high-B.t.u. gas has been produced in one reactor using sprayed plates in the hot gas recycle process, it is not completely satisfactory according to the specifications. More tests are necessary to determine the optimum operating conditions to make a gas to meet this standard.

This technique of flame spraying catalysts on inert forms may have applications to other processes than hydrocarbon synthesis. Many metals and metal oxides can be sprayed. It is possible by proper technique to remove the base metal from the sprayed material and have a shape composed entirely of the catalyst.

REFERENCES

1. Bienstock, D., J. H. Field, A. J. Forney, and R. J. Demski, Pilot Plant Development of the Hot-Gas-Recycle Process for the Synthesis of High-B.t.u. Gas. BuMines Rept. of Investigations 5841, 1961, 27 pp.

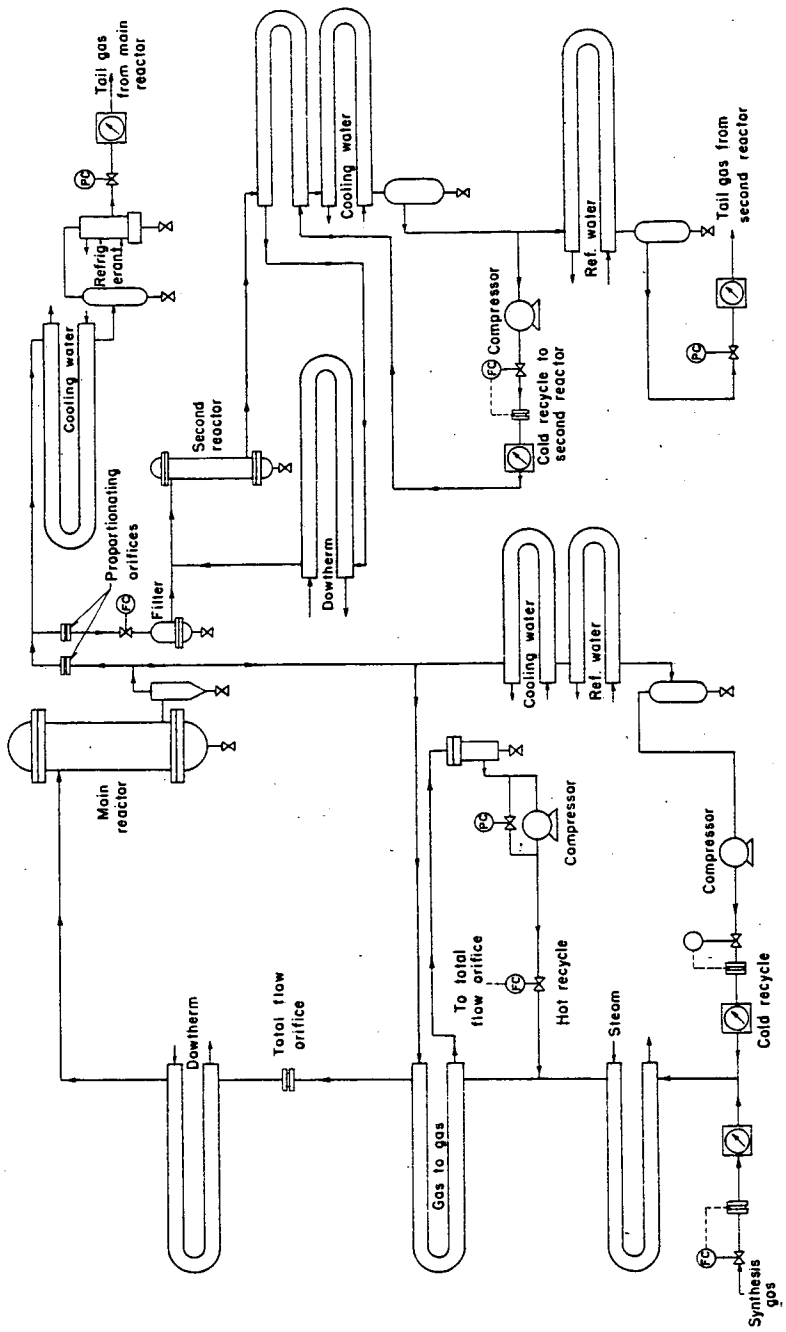

Figure 1. Flowsheet of hot gas recycle process for high-B.t.u. gas production.

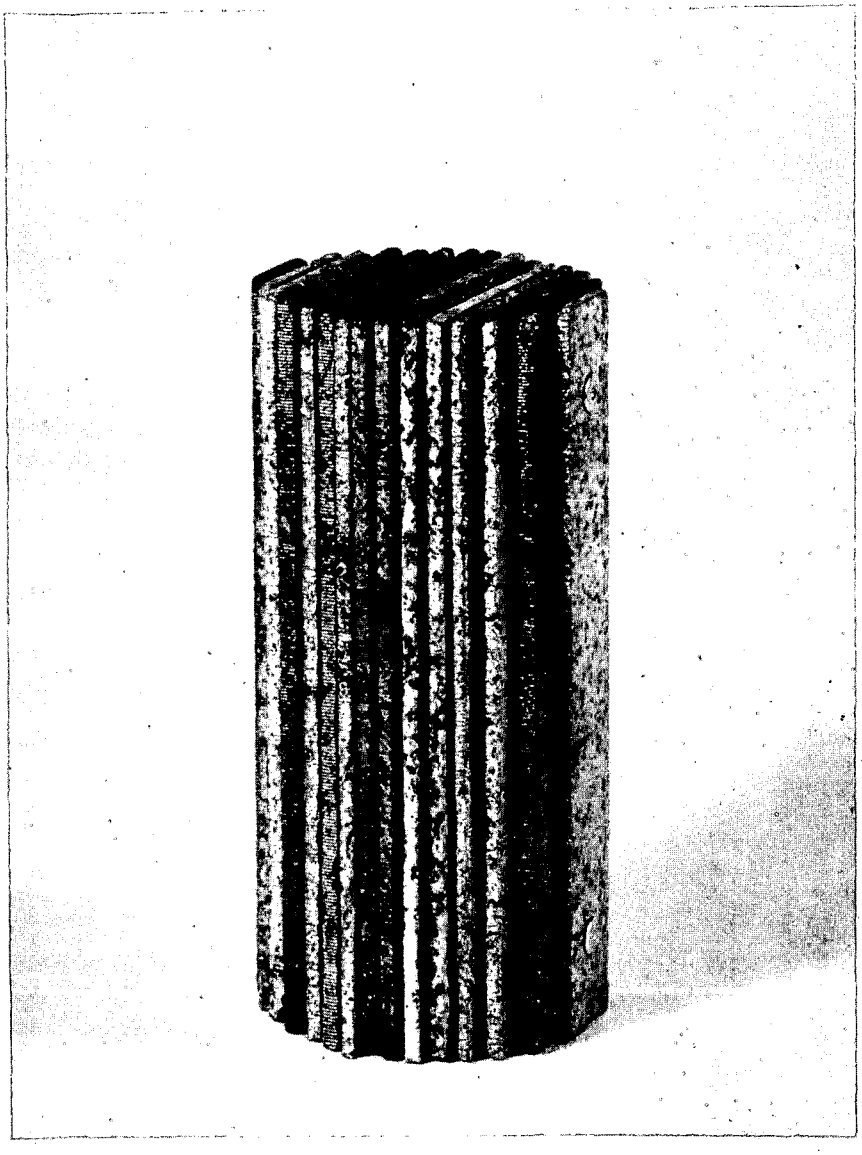

Figure 2. Parallel plate assembly of Raney nickel catalyst.